# Appendix 3

# Properties of Biomass[1]

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[1] Updated from Graboski, M. S. and Bain R. L. (1979). "Chapter 3: Properties of Biomass Relevant to Gasification," in A Survey of Biomass Gasification, Volume II - Principles of Gasification, Solar Energy Research Inst., Golden, CO, SERI/TR-33-239, July

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# PROPERTIES OF BIOMASS RELEVANT TO GASIFICATION

An understanding of the structure and properties of biomass materials is necessary to evaluate their utility as feedstocks for conversion processes.  This section summarizes available information on a variety of such properties including chemical analysis, heats of combustion and formation, physical structure, heat capacities, and transport properties of biomass feedstocks and chars.  Much of the information reported is for wood materials; however, where data were available for other forms of biomass such as municipal solid waste and feedlot waste, they were included.

## 3.1    BULK CHEMICAL ANALYSIS OF BIOMASS

In evaluating gasification feedstocks, it is generally useful to have proximate and ultimate analyses, heats of combustion, and sometimes ash analyses.  These provide information on volatility of the feedstock, elemental analysis, and heat content.  The elemental analysis is particularly important in evaluating the feedstock in terms of potential pollution.

Table 3-1 lists the standard Methods for evaluating carbonaceous feedstocks.

A number of instruments have been developed for determining elemental composition, most often, in biomass conversion, for carbon, hydrogen, nitrogen, sulfur, and oxygen.  Chlorine normally is not determined by such analyzers.  Most of these systems employ a catalytic combustion or pyrolysis step to decompose the sample to carbon dioxide, water, hydrogen sulfide, and nitrogen, which are then determined quantitatively by as chromatography using flame ionization (FID) or thermal conductivity (TC) detectors.  Oxygen is usually determined by catalytic conversion to carbon monoxide over a platinized carbon catalyst followed by GC analysis.  A short list of some representative equipment is given in Table 3-2.

### 3.1.1  Proximate Analyses

The proximate analysis classifies the fuel in terms of its moisture (M), volatile matter (VM), ash, and (by difference) fixed carbon content.  In the test procedure, the volatile material is driven off in an inert atmosphere at high temperatures (950°C) using a slow heating rate.  The pyrolysis yield is representative of that for slow pyrolysis processes; fast pyrolysis techniques employing very rapid heating rates normally yield more volatile matter.  The moisture determined by the proximate method represents physically bound water only; water released by chemical reactions during pyrolysis is classified with the volatiles.  The ash content is determined by combustion of the volatile and fixed carbon fractions.  The resulting ash fraction is not representative of the original ash, more appropriately termed mineral matter, due to the oxidation process employed in its determination.  In the most exact analysis, small corrections to the ash weight are necessary to correct it to a mineral

**Table 3-1:  ASTM Standards Methods for Biomass and Coal**

| Method | Biomass Test No. | Coal Test No. | Repeatability[a] (wt%) | Reproducibility[b] (wt%) |
|---|---|---|---|---|
| Proximate Analysis | | | | |
| Moisture | E871 | D2013, D3173 | 0.5 | 1.0 |
| Volatile Matter | E872, E897 | D3175 | 0.5 | 1.0 |
| Ash | D1102, E830 | D3174 | 0.6 | 1.3 |
| Fixed Carbon | Difference | Difference | | |
| Ultimate Analysis | | D3176 | | |
| C | E777 | D3176 | 0.5 | 1.6 |
| H | E777 | D3178 | 0.2 | 0.5 |
| N | E778 | D3179 | 0.04 | 0.05 |
| S | E775 | D4239, D3177 | 0.03 | 0.06 |
| O | Difference | Difference | | |
| Chlorine | E776 | D2361 | 0.03 | 0.11 |
| Gross Heating Value | E711, D2015 | D2015 | 27-111 Btu/lb[c] | 68-250 Btu/lb[c] |
| Ash Analysis | | | | |
| Ash in Biomass | E1755 | | 2.7[d] | 8.9[d] |
| Ash in wood | D1102 | | 0.03 (6.6[d]) | |
| Elemental Ash | D3682, D2795 | | 5[d] See element | |
| Fusion temp | D1857 | | 50°F | |
| Water soluble alkali | Soak overnight in $H_2O$ @90 C, Analyze by AA | | | |
| Bulk Density | E873 | | TBD | TBD |
| Fuel size (based on RDF) | E828 | | | |

[a] within laboratory; [b] between laboratories; [c] dependent on magnitude of HHV
[d] % of average

matter basis.  The fixed-carbon content of an as received sample is calculated by material balance.  Thus:

$$FC = 1 - M - ASH - VM \qquad (3\text{-}1)$$

The fixed carbon is considered to be a polynuclear aromatic hydrocarbon residue resulting from condensation reactions which occur in the pyrolysis step.

**Table 3-2:  Elemental Analyzer Equipment**

| Instrument | Oxidant | Capability | Detection |
|---|---|---|---|
| Carlo Erba 1104 | oxygen | C, H, N, O | FID & TIC |
| Chemical Data Systems (CDS 1200) | oxygen | C, H, N, O, S and functional groups | FID & TC |
| Hewlett-Packard HP-185 | $MNO_2$ added | C, H, N | FID & TC |
| Perkin Elmer 240 | oxygen | C, H, N, O, S | TC |

The most useful basis for reporting proximate analysis is the dry basis.  In this instance the compositions are normalized to a moisture-free basis (denoted by *):

$$VM^* + FC^* + ASH \ = \ 1, \qquad (3\text{-}2)$$

and, for example,

$$VM^* = VM/(1\text{-}M).$$

The moisture is reported as grams of moisture per gram of dry feedstock.  Typical proximate analyses for solid fuels are given in Table 3-3, from which it is evident that common biomass materials are more readily devolatilized (pyrolyzed) than lignite and bituminous coals, yielding considerably less fixed-carbon residue.  This is due to the much more aromatic structure of the coals which is produced by the geological coalification process.  The higher volatile content of biomass materials makes them potentially useful feedstocks for pyrolysis processes.  In general, the ash content of biomass materials is considerably lower than for coals.  This is due to the fact that the bulk of the coal ash was deposited in coal beds by processes such as siltation and did not come from the parent carbonaceous material.  An exception is municipal solid waste, which contains a high mineral content due to nonvolatile trash components such as metals and glass.

**Table 3-3: Proximate Analysis Data for Selected Solid Fuels and Biomass**
(Dry basis, wt%)

| | Volatile Matter (VM) | Fixed Carbon (FC) | Ash | Reference |
|---|---|---|---|---|
| **Coals** | | | | |
| Pittsburgh seam | 33.9 | 55.8 | 10.3 | Bituminous Coal Research 1974 |
| Wyoming Elkol | 44.4 | 51.4 | 4.2 | |
| Lignite | 43.0 | 46.6 | 10.4 | |
| | | | | |
| **Oven Dry Woods** | | | | |
| Western hemlock | 84.8 | 15.0 | 0.2 | Howlett and Gamanche 1977 |
| Douglas fir | 86.2 | 13.7 | 0.1 | |
| White fir | 84.4 | 15.1 | 0.5 | |
| Ponderosa pine | 87.0 | 12.8 | 0.2 | |
| Redwood | 83.5 | 16.1 | 0.4 | |
| Cedar | 77.0 | 21.0 | 2.0 | |
| | | | | |
| **Oven Dry Barks** | | | | |
| Western hemlock | 74.3 | 24.0 | 1.7 | Howlett and Gamance 1977 |
| Douglas fir | 70.6 | 27.2 | 2.2 | |
| White fir | 73.4 | 24.0 | 2.6 | |
| Ponderosa pine | 73.4 | 25.9 | 0.7 | |
| Redwood | 71.3 | 27.9 | 0.8 | |
| Cedar | 86.7 | 13.1 | 0.2 | |
| | | | | |
| **Municipal Refuse and Major Components** | | | | |
| Nat'l Ave. Waste | 65.9 | 9.1 | 25.0 | Klass and Ghosh 1973 |
| Newspaper (9.4%) | 86.3 | 12.2 | 1.5 | |
| Paper boxes (23.4%) | 81.7 | 12.9 | 5.4 | |
| Magazine paper (6.8%) | 69.2 | 7.3 | 23.4 | |
| Brown paper (5.6%) | 89.1 | 9.8 | 1.1 | |
| | | | | |
| **Selected Biomass** | | | | |
| Almond wood | 77.28 | 15.94 | 6.78 | Miles et. al. 1995 |
| Red oak sawdust | 86.22 | 13.47 | 0.31 | |
| Hybrid poplar | 84.81 | 12.49 | 2.70 | |
| Alfalfa stems | 78.92 | 15.81 | 5.27 | |
| Wheat straw, Denmark | 69.80 | 12.29 | 10.78 | |
| Wheat straw, OR | 81.24 | 17.06 | 4.32 | |
| Rice straw | 65.47 | 15.86 | 18.67 | |
| Willow | 85.23 | 13.82 | 0.95 | |
| Sugar cane bagasse | 85.61 | 11.95 | 2.44 | |
| Switchgrass, MN | 82.94 | 14.37 | 2.69 | |
| Bana Grass | 73.44 | 16.68 | 9.88 | |

### 3.1.2 <u>Ultimate Analyses</u>

Ultimate analyses generally report C, H, N, S and O (by difference ) in the solid fuel. Table 3-1 lists the appropriate ASTM tests for these elements while Table 3-2 lists several manufacturers of modern elemental analyzers. Care must be exercised in using ultimate analyses for fuels containing high moisture content because moisture is indicated in the ultimate analysis as additional hydrogen and oxygen.

To avoid confusion and give a good representation of the fuel itself, ultimate analyses should be performed and reported on a dry basis; when this is done all hydrogen determined is truly a constituent of the fuel. For certain biomass materials like municipal solids and animal waste, the determination of chlorine is important because it represents a possible pollutant and corrosive agent in gasification and combustion systems.

Typical ultimate analyses for a variety of feedstocks are presented in Table 3-4.

All biomass materials have carbon contents considerably lower than coals; the atomic carbon to hydrogen ratio is much higher in coals than in biomass materials. For coal, the H/C ratio is unity, while for biomass the ratio is typically 1.5. The bound oxygen content of biomass materials is considerably higher, due to the ether, acid, and alcohol groups in the cellulose, hemicellulose, and lignin fractions of biomass, as will be discussed later in this section. The nitrogen and sulfur contents in coal are considerably higher than those in most biomass. Thus, in direct biomass combustion, pollutants resulting from bound nitrogen and sulfur in the fuel generally are present in small enough quantities to meet EPA standards, although the high chlorine contents that are found in animal wastes can pose a severe pollution problem. The nitrogen content, normalized by heating value, of selected samples from Table 3-4 is given in Figure 3-1. Alkali content of biomass is important also because of its potential impact on slagging and fouling in combustion and gasification systems. A recent study (Miles 1995) found that biomass feeds containing less than 0.5 lb K per million Btu did not cause fouling and slagging in commercial biomass boilers. The potassium content of selected biomass samples from Table 3-4 is shown in Figure 3-2.

The relative "quality" of the volatile matter can be estimated using the ultimate analysis and simple stoichiometry. If it is assumed that the fixed carbon contains only carbon, then all hydrogen and oxygen plus a portion of the carbon are associated with the volatile materials. Table 3-5 presents a typical calculation for the volatile fraction of lignite and Douglas fir bark.

## Table 3-4: Ultimate Analysis Data for Selected Solid Fuels and Biomass Materials
(Dry basis, wt %)

| Material | C | H | N | S | O | Cl | Ash | HHV Btu/lb | HHV MJ/kg | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Pittsburgh seam coal | 75.5 | 5.0 | 1.2 | 3.1 | 4.9 | -- | 10.3 | 13,650 | 31.68 | Tillman 1978 |
| West Kentucky No. 11 coal | 74.4 | 5.1 | 1.5 | 3.8 | 7.9 | -- | 7.3 | 13,460 | 31.24 | Bituminous Coal Research 1974 |
| Utah coal | 77.9 | 6.0 | 1.5 | 0.6 | 9.9 | -- | 4.1 | 14,170 | 32.89 | Tillman 1978 |
| Wyoming Elkol coal | 71.5 | 5.3 | 1.2 | 0.9 | 16.9 | -- | 4.2 | 12,710 | 29.50 | Bituminous Coal Research 1974 |
| Lignite | 64.0 | 4.2 | 0.9 | 1.3 | 19.2 | -- | 10.4 | 10,712 | 24.86 | Bituminous Coal Reseach 1974 |
| Charcoal | 80.3 | 3.1 | 0.2 | 0.0 | 11.3 | -- | 3.4 | 13,370 | 31.03 | Tillman 1978 |
| Alder, red | 49.55 | 6.06 | 0.13 | 0.07 | 43.78 | | 0.40 | 8,578 | 19.91 | Rossi |
| Alder/fir sawdust | 51.02 | 5.80 | 0.46 | 0.05 | 68.54 | 0.02 | 4.13 | 8,760 | 20.33 | Miles et. al. 1995 |
| Alfalfa Pellets | 44.90 | 5.60 | 2.90 | 0.22 | 37.08 | 0.39 | 9.30 | 7,807 | 18.12 | MN Project |
| Alfalfa Pellets | 45.60 | 5.50 | 2.70 | 0.21 | 36.99 | 0.39 | 9.00 | 7,880 | 18.29 | MN Project |
| Alfalfa seed straw | 46.76 | 5.40 | 1.00 | 0.02 | 40.72 | | 7.25 | 7,949 | 18.45 | Jenkins and Ebeling |
| Almond hulls | 45.79 | 5.36 | 0.96 | 0.01 | 40.60 | | 5.78 | 7,850 | 18.22 | Jenkins and Ebeling |
| Almond prunings | 51.30 | 5.29 | 0.66 | 0.01 | 40.90 | | 1.63 | 8,621 | 20.01 | Jenkins and Ebeling |
| Almond shells | 44.98 | 5.97 | 1.16 | 0.02 | 42.27 | | 4.81 | 8,350 | 19.38 | Jenkins and Ebeling |
| Almond wood | 47.45 | 5.53 | 0.59 | 0.08 | 39.57 | 0.03 | 6.78 | 6,829 | 15.85 | Miles et. al. 1995 |
| Animal waste | 42.7 | 5.5 | 2.4 | 0.3 | 31.3 | | 17.8 | 7,380 | 17.13 | Tillman 1978 |
| Ash, white | 49.70 | 6.90 | | | 43.00 | | 0.30 | 8,940 | 20.75 | Johnson and Auth |
| Bagasse | 39.70 | 5.50 | 0.30 | | 42.30 | | 13.30 | 6,756 | 15.68 | Mudge et al |
| Bagasse | 44.80 | 5.35 | 0.38 | 0.01 | 39.55 | | 11.27 | 7,467 | 17.33 | Jenkins and Ebeling |
| Bagasse | 46.27 | 5.27 | 0.12 | 0.05 | 42.41 | 0.05 | 5.83 | 7,885 | 18.30 | Turn et. al. |
| Bagasse | 48.64 | 5.87 | 0.16 | 0.04 | 42.85 | 0.03 | 2.44 | 8,166 | 18.95 | Miles et. al. 1995 |
| Bagasse | 45.71 | 5.89 | | | 40.37 | | 8.03 | 8,402 | 19.50 | Grover and Anuradha |
| Bana Grass, HI | 45.06 | 5.42 | 0.84 | 0.11 | 38.69 | 0.83 | 9.88 | 7,533 | 17.48 | Miles et. al. 1995 |
| Banagrass | 47.10 | 5.29 | 0.44 | 0.16 | 41.93 | 0.61 | 4.47 | 7,897 | 18.33 | Turn et. al. |
| Bark | 47.27 | 5.20 | 0.40 | 0.05 | 37.68 | 0.03 | 9.37 | 7,721 | 17.92 | Feldman et. al. |
| Bean straw | 42.97 | 5.59 | 0.83 | 0.01 | 44.93 | | 5.93 | 7,523 | 17.46 | Jenkins and Ebeling |
| Beech | 51.6 | 6.3 | 0.0 | 0.0 | 41.5 | | 0.6 | 8,760 | 20.33 | Tillman 1978 |
| Birch and maple mix | 49.86 | 6.12 | 0.10 | 0.09 | 43.45 | 0.03 | 0.36 | 8,453 | 19.62 | Feldman et. al. |
| Birch, white | 49.80 | 6.50 | | | 43.40 | | 0.30 | 8,669 | 20.12 | Johnson and Auth |

| Material | C | H | N | S | O | Cl | Ash | HHV Btu/lb | HHV MJ/kg | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Black locust | 50.73 | 5.71 | 0.57 | 0.01 | 41.93 | | 0.80 | 8,492 | 19.71 | Jenkins and Ebeling |
| Black walnut prunings | 49.80 | 5.82 | 0.22 | 0.01 | 43.25 | | 0.78 | 8,544 | 19.83 | Jenkins and Ebeling |
| Cabernet Sauvignon prunings | 46.59 | 5.85 | 0.83 | 0.04 | 43.90 | | 2.17 | 8,199 | 19.03 | Jenkins and Ebeling |
| Casuarina | 48.50 | 6.04 | 0.31 | 0.00 | 43.32 | | 1.83 | 8,087 | 18.77 | Channiwala |
| Casuarina | 48.61 | 5.83 | 0.59 | 0.02 | 43.36 | | 1.40 | 8,376 | 19.44 | Jenkins and Ebeling |
| Cedar bark | 51.00 | 5.70 | | | 38.20 | | 5.10 | 8,630 | 20.03 | Johnson and Auth |
| Cedar, white | 48.80 | 6.40 | | | 44.40 | | 0.40 | 8,018 | 18.61 | Johnson and Auth |
| Chaparall | 46.90 | 5.08 | 0.54 | 0.03 | 40.17 | | 6.13 | 8,337 | 19.35 | Jenkins and Ebeling |
| Chenin Blanc prunings | 48.02 | 5.89 | 0.86 | 0.07 | 41.93 | | 2.51 | 8,242 | 19.13 | Jenkins and Ebeling |
| Cherry | 48.52 | 5.81 | 0.31 | 0.02 | 42.97 | 0.02 | 1.35 | 8,408 | 19.51 | Feldman et. al. |
| Chinkapin | 49.68 | 5.93 | 0.07 | 0.01 | 44.03 | | 0.30 | 8,337 | 19.35 | Rossi |
| Christmas trees | 51.59 | 5.58 | 0.52 | 0.40 | 36.70 | -- | 5.21 | 9,009 | 20.91 | Miles et. al. 1995 |
| Cocoa hulls | 48.23 | 5.23 | 2.98 | 0.12 | 33.19 | | 8.25 | 8,203 | 19.04 | Jenkins and Ebeling |
| Coconut fiber (coir) | 50.29 | 5.05 | 0.45 | 0.16 | 39.63 | | 3.72 | 8,639 | 20.05 | Channiwala |
| Coconut shells | 50.22 | 5.07 | 0.00 | 0.00 | 43.37 | | 0.71 | 8,832 | 20.50 | Channiwala |
| Corn cobs | 46.58 | 5.87 | 0.47 | 0.11 | 45.46 | | 1.36 | 8,087 | 18.77 | Jenkins and Ebeling |
| Corn stover | 43.65 | 5.56 | 0.61 | 0.01 | 43.31 | | 5.58 | 7,604 | 17.65 | Jenkins and Ebeling |
| Corn Stover | 46.50 | 5.81 | 0.56 | 0.11 | 39.67 | | 7.40 | 8,186 | 19.00 | Gregory et al |
| Corn stover | 46.51 | 5.81 | 0.56 | 0.11 | 39.67 | | 7.00 | 8,782 | 20.38 | Evans et. al. |
| Cotton gin trash | 39.59 | 5.26 | 2.09 | 2.09 | 36.38 | | 17.60 | 7,075 | 16.42 | Jenkins and Ebeling |
| Cotton gin waste | 42.66 | 6.05 | 0.18 | | 49.50 | | 1.61 | 7,531 | 17.48 | Channiwala |
| Cotton stalk | 39.47 | 5.07 | 1.25 | 0.02 | 38.09 | | 17.20 | 6,820 | 15.83 | Channiwala |
| Cotton stalk | 43.64 | 5.81 | 0.00 | 0.00 | 43.87 | | 6.68 | 7,867 | 18.26 | Grover and Anuradha |
| Cypress | 55.00 | 6.50 | | | 38.10 | | 0.40 | 9,892 | 22.96 | Johnson and Auth |
| Demolition wood | 46.30 | 5.39 | 0.57 | 0.12 | 34.50 | 0.05 | 13.12 | 7,916 | 18.37 | Miles et. al. 1995 |
| Douglas fir | 50.64 | 6.18 | 0.06 | 0.02 | 43.00 | | 0.10 | 8,837 | 20.51 | Rossi |
| Douglas fir | 52.3 | 6.3 | 0.1 | 0.0 | 40.5 | | 0.8 | 9,050 | 21.01 | Tillman 1978 |
| Douglas fir bark | 56.2 | 5.9 | 0.0 | 0.0 | 36.7 | | 1.2 | 9,500 | 22.05 | Tillman 1978 |
| Elm | 50.40 | 6.60 | | | 42.30 | | 0.70 | 9,039 | 20.98 | Johnson and Auth |
| Eucalyptus Camaldulensis | 49.00 | 5.87 | 0.30 | 0.01 | 43.97 | | 0.76 | 8,367 | 19.42 | Jenkins and Ebeling |
| Eucalyptus Globulus | 48.18 | 5.92 | 0.39 | 0.01 | 44.18 | | 1.10 | 8,285 | 19.23 | Jenkins and Ebeling |
| Eucalyptus Grandis | 48.33 | 5.89 | 0.15 | 0.01 | 45.13 | | 0.52 | 8,337 | 19.35 | Jenkins and Ebeling |

| Material | C | H | N | S | O | Cl | Ash | HHV Btu/lb | HHV MJ/kg | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Fir mill waste | 51.23 | 5.98 | 0.06 | 0.03 | 42.29 | 0.19 | 0.41 | 8,779 | 20.38 | Miles et. al. 1995 |
| Fir, white | 49.00 | 5.98 | 0.05 | 0.01 | 44.75 | | 1.52 | 8,367 | 19.42 | Jenkins and Ebeling |
| Forest residuals | 50.31 | 4.59 | 1.03 | 0.11 | 39.99 | 0.04 | 3.97 | 8,670 | 20.12 | Miles et. al. 1995 |
| Furniture waste | 49.87 | 5.91 | 0.29 | 0.03 | 40.29 | <0.01 | 3.61 | 8,658 | 20.10 | Miles et. al. 1995 |
| Grape pomice | 54.94 | 5.83 | 2.09 | 0.21 | 32.08 | | 4.20 | 9,393 | 21.80 | Grover and Anuradha |
| Groundnut shells | 48.59 | 5.64 | 0.58 | 0.00 | 39.49 | | 5.70 | 8,552 | 19.85 | Johnson and Auth |
| Gum | 50.88 | 6.06 | 0.15 | 0.04 | 41.57 | 0.02 | 1.28 | 8,475 | 19.67 | Feldman et. al. |
| Hardwood | 49.73 | 6.06 | 0.24 | 0.04 | 42.87 | 0.11 | 0.95 | 8,430 | 19.57 | Feldman et. al. |
| Hemlock, western | 50.4 | 5.8 | 0.1 | 0.1 | 41.4 | | 2.2 | 8,620 | 20.01 | Tillman 1978 |
| Hickory | 49.7 | 6.5 | 0.0 | 0.0 | 43.1 | | 0.7 | 8,670 | 20.12 | Tillman 1978 |
| Hog fuel | 45.36 | 5.63 | 0.18 | 0.02 | 42.13 | 0.03 | 16.89 | 7,681 | 17.83 | Feldman et. al. |
| Kelp, brown, Soquel Point | 27.80 | 3.77 | 4.63 | 1.05 | 23.69 | | 42.10 | 4,632 | 10.75 | Chynoweth et al |
| Kelp, giant brown, Monterey | 26.60 | 3.74 | 2.55 | 1.09 | 20.22 | | 45.80 | 4,421 | 10.26 | Chynoweth et al |
| Macadamia shells | 54.41 | 4.99 | 0.36 | 0.01 | 39.69 | | 0.40 | 9,052 | 21.01 | Jenkins and Ebeling |
| Madrone | 48.56 | 6.05 | 0.05 | 0.02 | 45.08 | | 0.30 | 8,246 | 19.14 | Rossi |
| Madrone | 48.94 | 6.03 | 0.05 | 0.02 | 41.74 | | 0.20 | 8,406 | 19.51 | Rossi |
| Mango wood | 46.24 | 6.08 | 0.28 | | 44.42 | | 2.98 | 8,259 | 19.17 | Johnson and Auth |
| Manzanita | 48.18 | 5.95 | 0.17 | 0.02 | 44.68 | | 0.82 | 8,315 | 19.30 | Jenkins and Ebeling |
| Maple | 49.54 | 6.11 | 0.10 | 0.02 | 49.54 | | 0.50 | 8,306 | 19.28 | Evans et. al. |
| Maple | 50.6 | 6.0 | 0.3 | 0.0 | 41.7 | | 1.4 | 8,580 | 19.91 | Tillman 1978 |
| Millet straw | 43.71 | 5.85 | 0.01 | 0.00 | 45.16 | | 5.27 | 7,777 | 18.05 | Channiwala |
| Mixed waste paper | 47.99 | 6.63 | 0.14 | 0.07 | 36.84 | | 8.33 | 8,934 | 20.74 | Miles et. al. 1995 |
| Mixed wood | 49.31 | 6.03 | 0.18 | 0.02 | 42.98 | 0.04 | 1.44 | 8,366 | 19.42 | Feldman et. al. |
| Mixed wood (90% red oak) | 48.51 | 6.17 | 0.12 | 0.04 | 44.22 | | 0.94 | 8,210 | 19.06 | Evans et. al. |
| Mixed wood | 48.40 | 6.31 | 0.21 | 0.03 | 44.23 | | 0.82 | 8,228 | 19.10 | Evans et. al. |
| Municipal solid waste | 47.6 | 8.0 | 1.2 | 0.3 | 32.9 | | 12.0 | 8,546 | 19.84 | Saner et. al. 1970 |
| Napier grass | 45.20 | 6.00 | | | 42.30 | | 5.70 | 7,889 | 18.31 | Elliot et al |
| Oak | 49.83 | 5.87 | 0.32 | 0.04 | 41.82 | 0.03 | 2.09 | 8,373 | 19.43 | Feldman et. al. |
| Oak, Alabama woodwaste | 49.5 | 5.7 | 0.2 | 0.0 | 41.3 | -- | 3.3 | 8,266 | 19.19 | Boley and Landers 1969 |
| Oak, Canyon | 47.84 | 5.80 | 0.07 | 0.01 | 45.76 | | 0.50 | 8,178 | 18.98 | Rossi |
| Oak, red | 49.34 | 5.93 | 0.07 | 0.13 | 41.74 | 0.03 | 2.76 | 8,220 | 19.08 | Feldman et. al. |
| Oak, red, sawdust | 49.96 | 5.92 | 0.03 | 0.01 | 43.77 | 0.07 | 0.31 | 8,374 | 19.44 | Miles et. al. 1995 |

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| Material | C | H | N | S | O | Cl | Ash | HHV Btu/lb | HHV MJ/kg | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Oak, tan | 48.67 | 6.03 | 0.06 | 0.04 | 44.99 | | 0.20 | 8,156 | 18.93 | Rossi |
| Oak, tan | 48.34 | 6.12 | 0.03 | 0.03 | 44.99 | | 0.50 | 8,238 | 19.12 | Jenkins and Ebeling |
| Oak, white | 49.48 | 5.38 | 0.35 | 0.01 | 43.13 | | 1.52 | 8,367 | 19.42 | Jenkins and Ebeling |
| Olive pits | 48.81 | 6.23 | 0.36 | 0.01 | 43.48 | | 3.20 | 9,216 | 21.39 | Channiwala |
| Paper | 43.4 | 5.8 | 0.3 | 0.2 | 44.3 | -- | 6.0 | 7,572 | 17.57 | Bowernan 1969 |
| Peach pits | 49.14 | 6.34 | 0.48 | 0.02 | 43.52 | | 1.10 | 8,367 | 19.42 | Rossi |
| Peach pits | 53.00 | 5.90 | 0.32 | 0.05 | 39.14 | | 1.03 | 8,970 | 20.82 | Jenkins and Ebeling |
| Peanut hulls | 45.77 | 5.46 | 1.63 | 0.12 | 39.56 | | 5.89 | 8,031 | 18.64 | Jenkins and Ebeling |
| Pine | 51.27 | 6.19 | 0.13 | 0.13 | 42.13 | 0.02 | 0.13 | 8,748 | 20.30 | Feldman et. al. |
| Pine bark | 52.3 | 5.8 | 0.2 | 0.0 | 38.8 | | 2.9 | 8,780 | 20.38 | Tillman 1978 |
| Pine needles | 48.21 | 6.57 | | | 43.72 | | 1.50 | 8,669 | 20.12 | Grover and Anuradha |
| Pine, long leaf, bark | 56.40 | 5.50 | | | 37.40 | | 0.70 | 9,380 | 21.77 | Risser |
| Pine, ponderosa | 49.25 | 5.99 | 0.06 | 0.03 | 44.36 | | 0.29 | 8,470 | 19.66 | Jenkins and Ebeling |
| Pine, slash, bark | 56.20 | 5.40 | | | 37.30 | | 0.70 | 9,380 | 21.77 | Risser |
| Pine, white | 52.60 | 6.10 | | | 41.20 | | 0.10 | 8,919 | 20.70 | Johnson and Auth |
| Pine, yellow | 52.60 | 7.00 | | | 52.60 | | 1.31 | 9,668 | 22.44 | Riser |
| Pine. Loblolly, bark | 56.30 | 5.60 | | | 37.70 | | 0.40 | 9,384 | 21.78 | Risser |
| Pistachio shells | 48.79 | 5.91 | 0.56 | 0.01 | 43.41 | | 1.13 | 8,298 | 19.26 | Jenkins and Ebeling |
| Poplar | 48.45 | 5.85 | 0.47 | 0.01 | 43.69 | | 1.33 | 8,350 | 19.38 | Jenkins and Ebeling |
| Poplar | 51.6 | 6.3 | 0.0 | 0.0 | 41.5 | | 0.6 | 8,920 | 20.70 | Tillman 1978 |
| Poplar - coarse | 50.82 | 5.89 | 0.59 | 0.02 | 41.08 | 0.04 | 1.60 | 8,139 | 18.89 | Miles et. al. 1995 |
| Poplar, hybrid | 50.18 | 6.06 | 0.60 | 0.02 | 40.44 | 0.01 | 2.70 | 8,178 | 18.98 | Miles et. al. 1995 |
| Redwood | 53.5 | 5.9 | 0.1 | 0.0 | 40.3 | | 0.2 | 9,040 | 20.98 | Tillman 1978 |
| Redwood wastewood | 53.4 | 6.0 | 0.1 | 0.1 | 39.9 | | 0.6 | 9,163 | 21.27 | Boley and Landers 1969 |
| RDF - Tacoma, WA | 39.70 | 5.78 | 0.80 | 0.35 | 27.24 | | 26.13 | 6,679 | 15.50 | Miles et. al. 1995 |
| Rice hulls | 38.30 | 4.36 | 0.83 | 0.06 | 35.45 | | 20.60 | 6,415 | 14.89 | Rossi |
| Rice hulls | 38.5 | 5.7 | 0.5 | 0.0 | 39.8 | | 15.5 | 6,610 | 15.34 | Tillman 1978 |
| Rice husk | 38.92 | 5.10 | 2.17 | 0.12 | 37.89 | | 15.80 | 6,751 | 15.67 | Maheshwari |
| Rice husk bran | 39.82 | 5.12 | 0.55 | 0.00 | 36.77 | | 18.64 | 6,588 | 15.29 | Channiwala |
| Rice straw | 39.2 | 5.1 | 0.6 | 0.1 | 35.8 | | 19.2 | 6,540 | 15.18 | Tillman 1978 |
| Rice straw | 41.78 | 4.63 | 0.70 | 0.08 | 36.57 | | 13.42 | 7,014 | 16.28 | Jenkins and Ebeling |
| Sawdust | 51.33 | 6.13 | 0.12 | 0.02 | 41.97 | 0.07 | 0.36 | 8,802 | 20.43 | Feldman et. al. |

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| Material | C | H | N | S | O | Cl | Ash | HHV Btu/lb | HHV MJ/kg | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Sawdust pellets | 47.2 | 6.5 | 0.0 | 0.0 | 45.4 | | 1.0 | 8,814 | 20.46 | Wen et. al. 1974 |
| Shredded currency | 42.89 | 5.97 | 1.75 | 0.30 | 43.62 | | 5.47 | 7,867 | 18.26 | Miles et. al. 1995 |
| Softwood | 50.80 | 6.25 | 0.15 | 0.14 | 41.74 | 0.03 | 0.78 | 8,771 | 20.36 | Feldman et. al. |
| Southern oak | 49.94 | 5.30 | 0.16 | 0.00 | 42.77 | 0.02 | 0.81 | 8,500 | 19.73 | Feldman et. al. |
| Spruce | 51.80 | 5.70 | | | 38.30 | | 3.80 | 8,759 | 20.33 | Johnson and Auth |
| Sudan grass | 44.58 | 5.35 | 1.21 | 0.01 | 39.18 | | 8.65 | 7,492 | 17.39 | Jenkins and Ebeling |
| Switchgrass, Columbus, OH | 46.68 | 5.82 | 0.77 | 0.19 | 37.57 | 0.03 | 8.97 | 7,766 | 18.02 | Miles et. al. 1995 |
| Switchgrass, Dakota Leaf, MN | 47.45 | 5.75 | 0.74 | 0.08 | 42.37 | 0.03 | 3.61 | 8,014 | 18.60 | Miles et. al. 1995 |
| Switchgrass, G Petersen 1 | 48.64 | 5.46 | 0.04 | 0.07 | 42.06 | 0.005 | 3.73 | 8,001 | 18.57 | Iowa Project |
| Switchgrass, G Petersen 2 | 47.98 | 5.46 | 0.19 | 0.06 | 41.54 | 0.007 | 4.77 | 7,765 | 18.02 | Iowa Project |
| Switchgrass, G Petersen 4 | 48.37 | 5.52 | 0.03 | 0.15 | 43.59 | 0.003 | 2.34 | 8,104 | 18.81 | Iowa Project |
| Switchgrass, Joe Cross 1 | 47.11 | 5.39 | 0.23 | 0.06 | 43.19 | 0.007 | 4.02 | 7,934 | 18.41 | Iowa Project |
| Switchgrass, Joe Cross 2 | 46.00 | 4.57 | 0.32 | 0.05 | 44.51 | 0.006 | 4.54 | 7,862 | 18.25 | Iowa Project |
| Switchgrass, Joe Cross 4 | 48.00 | 5.54 | 0.16 | 0.07 | 42.61 | 0.004 | 3.61 | 8,017 | 18.61 | Iowa Project |
| Switchgrass, Krutsinger 1 | 46.91 | 5.38 | 0.38 | 0.07 | 41.61 | 0.017 | 5.64 | 7,890 | 18.31 | Iowa Project |
| Switchgrass, Krutsinger 2 | 44.97 | 5.10 | 0.69 | 0.09 | 42.43 | 0.024 | 6.72 | 7,812 | 18.13 | Iowa Project |
| Switchgrass, Krutsinger 4 | 48.20 | 5.68 | 0.24 | 0.06 | 42.00 | 0.017 | 3.81 | 7,952 | 18.46 | Iowa Project |
| Switchgrass, Lodge Land 1 | 47.71 | 5.43 | 0.38 | 0.04 | 41.53 | 0.007 | 4.91 | 7,953 | 18.46 | Iowa Project |
| Switchgrass, Lodge Land 2 | 47.46 | 5.41 | 0.48 | 0.05 | 43.18 | 0.007 | 3.42 | 8,091 | 18.78 | Iowa Project |
| Switchgrass, Lodge Land 4 | 47.72 | 5.48 | 0.15 | 0.06 | 43.10 | 0.003 | 3.49 | 8,034 | 18.65 | Iowa Project |
| Switchgrass, Schulz 30 | 48.69 | 5.61 | 0.06 | 0.05 | 43.14 | 0.003 | 2.44 | 8,012 | 18.60 | Iowa Project |
| Switchgrass, Sellers 1 | 48.69 | 5.50 | 0.34 | 0.06 | 41.28 | 0.004 | 4.14 | 8,021 | 18.62 | Iowa Project |
| Switchgrass, Sellers 2 | 48.31 | 5.52 | 0.29 | 0.09 | 42.59 | 0.005 | 3.20 | 8,074 | 18.74 | Iowa Project |
| Switchgrass, Sellers 32 | 49.10 | 5.71 | 0.17 | 0.05 | 42.21 | 0.002 | 2.76 | 7,983 | 18.53 | Iowa Project |
| Switchgrass, Sellers 4 | 48.72 | 5.54 | 0.16 | 0.05 | 41.70 | 0.008 | 3.83 | 8,052 | 18.69 | Iowa Project |
| Switchgrass, Summer, MN | 47.51 | 5.02 | 0.65 | 0.07 | 37.02 | 0.03 | 2.69 | 7,979 | 18.52 | Miles et. al. 1995 |
| Switchgrass, SWG10 | 43.78 | 5.25 | 0.52 | 0.07 | 46.10 | 0.035 | 4.29 | 7,806 | 18.12 | Iowa Project |
| Switchgrass, SWG12 | 43.20 | 5.23 | 0.50 | 0.10 | 47.19 | 0.046 | 3.78 | 7,735 | 17.95 | Iowa Project |
| Switchgrass, SWG14 | 42.13 | 5.07 | 0.54 | 0.08 | 48.49 | 0.022 | 3.68 | 7,803 | 18.11 | Iowa Project |
| Switchgrass, SWG16 | 42.89 | 5.05 | 0.57 | 0.10 | 47.68 | 0.015 | 3.71 | 7,837 | 18.19 | Iowa Project |
| Switchgrass, SWG18 | 43.93 | 5.17 | 0.55 | 0.08 | 46.86 | 0.005 | 3.41 | 7,809 | 18.12 | Iowa Project |
| Switchgrass, SWG20 | 44.21 | 5.07 | 0.64 | 0.09 | 46.23 | 0.004 | 3.75 | 7,793 | 18.09 | Iowa Project |

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| Material | C | H | N | S | O | Cl | Ash | HHV Btu/lb | HHV MJ/kg | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| Switchgrass, SWG22 | 44.45 | 5.14 | 0.59 | 0.11 | 46.17 | 0.004 | 3.53 | 7,847 | 18.21 | Iowa Project |
| Switchgrass, SWG26 | 44.86 | 5.15 | 0.57 | 0.09 | 46.20 | 0.005 | 3.13 | 7,852 | 18.22 | Iowa Project |
| Switchgrass, SWG28 | 44.71 | 5.15 | 0.63 | 0.07 | 45.90 | 0.003 | 3.55 | 7,785 | 18.07 | Iowa Project |
| Switchgrass, Van Patten 1 | 48.32 | 5.50 | 0.10 | 0.06 | 42.80 | 0.036 | 3.21 | 8,161 | 18.94 | Iowa Project |
| Switchgrass, Van Patten 2 | 48.41 | 5.48 | 0.09 | 0.04 | 42.56 | 0.024 | 3.42 | 8,091 | 18.78 | Iowa Project |
| Switchgrass, Van Patten 4 | 46.95 | 5.79 | 0.14 | 0.06 | 44.71 | 0.012 | 2.35 | 8,182 | 18.99 | Iowa Project |
| Switchgrass, WG24 | 44.03 | 5.09 | 0.55 | 0.09 | 46.30 | 0.006 | 3.93 | 7,864 | 18.25 | Iowa Project |
| Urban wood waste | 48.77 | 5.76 | 0.27 | 0.07 | 39.59 | 0.05 | 2.50 | 8,361 | 19.41 | Miles et. al. 1995 |
| Walnut shells | 49.98 | 5.35 | 0.21 | 0.01 | 43.35 | | 0.56 | 8,695 | 20.18 | Jenkins and Ebeling |
| Walnut, English, prunings | 49.72 | 5.63 | 0.37 | 0.01 | 43.14 | | 1.08 | 8,458 | 19.63 | Jenkins and Ebeling |
| Water hyacinth | 40.30 | 4.60 | 1.51 | | 33.99 | | 19.60 | 6,402 | 14.86 | Klass and Ghosh |
| Water hyacinth | 43.00 | 5.80 | 5.60 | | 29.50 | | 15.30 | 7,747 | 17.98 | Elliot et al |
| Wheat dust | 41.38 | 5.10 | 3.04 | 0.19 | 35.17 | | 13.68 | 6,980 | 16.20 | Jenkins and Ebeling |
| Wheat straw | 43.20 | 5.00 | 0.61 | 0.11 | 39.40 | | 8.90 | 7,199 | 16.71 | Jenkins and Ebeling |
| Willow - SA22 -3 yr | 49.90 | 5.90 | 0.61 | 0.07 | 41.81 | <0.01 | 1.71 | 8,424 | 19.55 | Miles et. al. 1995 |
| Willow - SA22 Butt | 48.95 | 6.05 | 0.36 | 0.04 | 43.54 | 0.01 | 1.06 | 8,326 | 19.32 | Miles et. al. 1995 |
| Willow - SA22 Top | 49.42 | 5.89 | 0.96 | 0.12 | 41.27 | <0.01 | 2.34 | 8,510 | 19.75 | Miles et. al. 1995 |
| Willow - SA22-1 yr | 49.75 | 6.00 | 0.65 | 0.09 | 42.01 | 0.01 | 1.50 | 8,457 | 19.63 | Miles et. al. 1995 |
| Willow - SH3-1 yr | 48.85 | 6.04 | 0.71 | 0.06 | 42.64 | 0.01 | 1.70 | 8,443 | 19.60 | Miles et. al. 1995 |
| Willow - SP3-1yr | 50.29 | 6.01 | 0.50 | 0.07 | 41.93 | <0.01 | 1.20 | 8,691 | 20.17 | Miles et. al. 1995 |
| Willow - SV1-1 yr | 47.94 | 5.84 | 0.63 | 0.06 | 44.43 | <0.01 | 1.10 | 8,325 | 19.32 | Miles et. al. 1995 |
| Willow - SV1-3 yr | 49.09 | 5.89 | 0.35 | 0.03 | 46.39 | <0.01 | 0.95 | 8,330 | 19.33 | Miles et. al. 1995 |
| Wood - land clearing | 42.32 | 5.02 | 0.33 | 0.06 | 35.77 | 0.02 | 16.50 | 7,408 | 17.19 | Miles et. al. 1995 |
| Wood - yard waste | 41.54 | 4.79 | 0.85 | 0.24 | 32.21 | 0.30 | 20.37 | 7,009 | 16.27 | Miles et. al. 1995 |

**Figure 3-1: Nitrogen Content of Selected Biomass Samples**

**Nitrogen Content of Biomass**

| Biomass Sample | Nitrogen (lb/MBtu) |
|---|---|
| Alfalfa stems | ~3.0 |
| Rice straw | ~1.35 |
| Wood - yard waste | ~1.2 |
| RFD - Tacoma | ~1.2 |
| Forest residuals | ~1.15 |
| Bana Grass, HI | ~1.1 |
| Switchgrass, OH | ~1.0 |
| Switchgrass, D Leaf, MN | ~0.9 |
| Almond wood | ~0.85 |
| Switchgrass, MN | ~0.8 |
| Rice husks | ~0.75 |
| Willow - SV1-1 yr | ~0.75 |
| Hybrid poplar | ~0.72 |
| Imperial wheat straw | ~0.72 |
| Poplar - coarse | ~0.7 |
| Demolition wood | ~0.7 |
| California wheat straw | ~0.57 |
| Oregon wheat straw | ~0.53 |
| Alder/fir sawdust | ~0.52 |
| Danish wheat straw | ~0.5 |
| Wood - land clearing | ~0.45 |
| Willow - SV1-3 yr | ~0.42 |
| Miscanthus, Silberfeder | ~0.4 |
| Furniture waste | ~0.35 |
| Urban wood waste | ~0.32 |
| Sugar Cane Bagasse | ~0.2 |
| Mixed waste paper | ~0.15 |
| Fir mill waste | ~0.07 |
| Red oak sawdust | ~0.03 |

Nitrogen (lb/MBtu)

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**Figure 3-2: Potassium Content of Selected Biomass Samples[3]**

**Potassium Content of Biomass**

| Sample | Potassium Content (lb/MBtu) |
|---|---|
| Rice straw | 2.95 |
| Imperial wheat straw | 2.4 |
| California wheat straw | 1.95 |
| Alfalfa stems | 1.55 |
| Oregon wheat straw | 1.15 |
| Switchgrass, OH | 1.1 |
| Rice husks | 0.9 |
| Danish wheat straw | 0.8 |
| Wood - yard waste | 0.7 |
| Almond wood | 0.52 |
| Wood - land clearing | 0.4 |
| Miscanthus, Silberfeder | 0.37 |
| Poplar - coarse | 0.33 |
| Forest residuals | 0.32 |
| Demolition wood | 0.3 |
| Switchgrass, D Leaf, MN | 0.28 |
| Hybrid poplar | 0.27 |
| Switchgrass, MN | 0.23 |
| Alder/fir sawdust | 0.23 |
| Willow - SV1-1 yr | 0.15 |
| Furniture waste | 0.13 |
| Willow - SV1-3 yr | 0.13 |
| Urban wood waste | 0.12 |
| Sugar Cane Bagasse | 0.11 |
| Red oak sawdust | 0.07 |
| RFD - Tacoma | 0.07 |
| Fir mill waste | 0.03 |
| Mixed waste paper | 0.01 |

Potassium Content (lb/MBtu)

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## Table 3-5:  Elemental Analysis of Volatiles Liberated by Pyrolysis for Two Selected Fuels

| Fuel | wt% in volatile, dry basis | | | Molar ratio volatile | | |
|---|---|---|---|---|---|---|
| | C | H | O | C | H | O |
| Lignite | 17.4 | 4.22 | 19.17 | 1 | 2.91 | 0.83 |
| Douglas fir bark | 23.4 | 5.9 | 36.7 | 1 | 3.03 | 1.17 |

The C/H/O ratios of these volatile fractions are very similar despite the difference in feedstock.  In the pyrolysis process, at relatively high temperatures,

$$\nearrow \quad CH_4 \tag{3-3}$$

$$Volatiles \quad \rightarrow \quad CO + CO_2 \tag{3-4}$$

$$\searrow \quad H_2O \tag{3-5}$$

If we assume that CO is produced exclusively we can calculate the product analysis from pyrolysis.

Therefore, assuming:

$$C + 4H \quad \rightarrow \quad CH_4 \tag{3-6}$$

$$2H + O \quad \rightarrow \quad H_2 \tag{3-7}$$

$$C + O \quad \rightarrow \quad CO, \tag{3-8}$$

let X be the moles of carbon converted to methane, Y the oxygen converted to water, and Z the carbon to CO.

The material balance equations yield:

$$X = [ \, 2 + (H/C) - 2 \, (O/C) \, ] / 6 \tag{3-9}$$

$$Z = 1 - X \tag{3-10}$$

$$Y = O/C - Z \tag{3-11}$$

In the calculation for methane it should be pointed out that as long as water-gas shift reaction equilibrium is attained, it makes no difference whether the non-hydrocarbon products are CO and $H_2O$ or a mixture of CO, $CO_2$, $H_2$, and $H_2O$.

Table 3-6 presents such an analysis on a dry basis of 100 lb of fuel.

**Table 3-6: Evaluation of Feedstocks for Pyrolysis by Material Balance Calculation**

| Fuel | SCF Gas 100lb dry feed | Mole Fractions | | | Lb C in $CH_4$ 100lb C in feed |
|---|---|---|---|---|---|
| | | $CH_4$ | CO | $H_2O$ | |
| Lignite | 754 | 0.395 | 0.334 | 0.271 | 14.7 |
| Douglas fir bark | 1196 | 0.277 | 0.341 | 0.382 | 18.7 |

The gas derived from lignite is higher in quality than that from the fir bark due to the bark's greater potential to form water. The quantity of gas produced is greater for the fir bark due to the greater quantity of volatiles present. The most important factor is the fraction of carbon converted to methane. The woody material shows a greater potential to form methane on a carbon feed basis, indicating that it is a higher quality feedstock for pyrolysis. This may be attributed to the higher degree of aromaticity exhibited in coals.

Table 3-7 presents ultimate analysis for typical pyrolysis chars derived from biomass feedstocks. Except for the municipal solid waste char, all contain considerable quantities of volatile constituents, including H and O, due to the low processing temperature.

The C/H and C/O ratios are greater in all chars than in the fresh feed materials. The high-temperature municipal waste char has been almost completely devolatized, as is evidenced by the low H and O contents.

### 3.1.3  Moisture Content of Fuels

Woody fuels and municipal solid waste samples are available with various moisture contents. The moisture is important in determining drying costs and as-received heat contents of the fuels.

Table 3-8 presents approximate ranges of moisture for typical biomass fuels. The effect of moisture on the recoverable heat is dramatic due to the heat requirements for vaporizing the moisture plus superheating the vapor.

## Table 3-7: Ultimate Analysis Data for Selected Pyrolysis Chars
(Dry Basis, Weight Percent)

| Material | C | H | N | S | O | Ash | HHV Btu/lb | HHV MJ/kg | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Fir bark char | 49.9 | 4.0 | 0.1 | 0.1 | 24.5 | 21.4 | 8,260 | 19.17 | Pober and Bauer 1977 |
| Rice hull char | 36.0 | 2.6 | 0.4 | 0.1 | 11.7 | 49.2 | 6,100 | 14.16 | Pober and Bauer 1977 |
| Grass straw char | 51.0 | 3.7 | 0.5 | 0.8 | 19.7 | 24.3 | 8,300 | 19.26 | Pober and Bauer 1977 |
| Animal waste char[a] | 34.5 | 2.2 | 1.9 | 0.9 | 7.9 | 48.8 | 5,450 | 12.65 | Pober and Bauer 1977 |
| MSW char | 54.9 | 0.8 | 1.1 | 0.2 | 1.8 | 41.2 | 8,020 | 18.61 | Sanner et al 1970 |
| Redwood charcoal (421 - 549°C) | 75.6 | 3.3 | 0.2 | 0.2 | 18.4 | 2.3 | 12,400 | 28.78 | Boley and Landers 1969 |
| Redwood charcoal (460 - 941°C) | 78.8 | 3.5 | 0.2 | 0.2 | 13.2 | 4.1 | 13,100 | 30.41 | Boley and Landers 1969 |
| Oak charcoal (438 - 641°C) | 67.7 | 2.4 | 0.4 | 0.2 | 14.4 | 14.9 | 10,660 | 24.60 | Boley and Landers 1969 |
| Oak charcoal (571°C) | 64.6 | 2.1 | 0.4 | 0.1 | 15.5 | 17.3 | 9,910 | 23.00 | Boley and Landers 1969 |

[a]Contains 3.7% Cl lumped with oxygen

**Table 3-8:  Approximate Moisture Contents Of Typical Biomass Fuels**

| Biomass Fuel | Moisture Content (wt %) |
|---|---|
| Bark | 25 - 75 |
| Coarse wood residue | 30 - 60 |
| Manure, beef cattle | 80 - 90 |
| Manure, poultry | 70 - 80 |
| Shavings | 16 - 40 |
| Sawdust | 25 - 40 |
| Sander dust | 2 - 8 |
| Municipal refuse | 20 |
| Air dry feedlot waste | 12 |
| Baled switchgrass | 10 - 15 |

### 3.1.4  Heating Values

The heating value of carbon feedstocks is determined by the ASTM method listed in Table 3-1.  The experimental method employs an adiabatic bomb calorimeter which measures the enthalpy change between reactants and products at 25°C.  The heating value obtained is termed the higher heating value because the water of combustion is present in the liquid state at the completion of the experimental determination.

The heating value may be reported on two bases.  These are the gross or higher heating value and the net or lower heating value.  The higher heating value (HHV) represents the heat of combustion relative to liquid water as the product.  The lower heating value (LHV) is based on gaseous water.  You may also see HHV and LHV referred to as gross calorific value (GCV) and net calorific value (NCV). The difference in the heating value is the latent heat of the water of combustion.  Heating values often are reported on both wet and dry fuel bases.  The conversion between bases is simple in the case of the higher heating value, involving only normalizing out the moisture (M). This is true because the moisture present in the raw fuel is in the same state before and after combustion.

$$HHV^* = HHV / (1 - M) \tag{3-12}$$

Lower (net) heating values depend on the moisture content in a more complicated

fashion. Since both the product water and moisture are present as vapor after combustion, a portion of the heat of combustion is used to evaporate the moisture. Therefore, using the latent heat of water, $\lambda = 980$ Btu/lb,

$$HHV^* = ( LHV - M\lambda ) / (1 - M) \qquad (3-13)$$

To convert between higher (gross) and lower (net) heating values, the amount of water produced by combustion reactions, but not including moisture, must be known. If this is called W, lb water/lb fuel, then the heating values are related by:

$$HHV = LLV + W\lambda. \qquad (3-14)$$

All heats reported in this discussion are higher (gross) heating values on a dry basis.

Table 3-4 reports higher heating values on a dry basis for a variety of biomass fuels. Typically, the heating values for coals are much greater than for biomass materials, ranging from 10 MBtu/lb to 14 MBtu/lb (23.2 MJ/kg to 32.5 MJ/kg) and 5 MBtu/lb to 9 MBtu/lb (11.6 MJ/kg to 20.9 MJ/kg), respectively. This is principally due to the higher carbon content of the coals. Table 3-7 gives higher heating values for biomass chars. The values are low due to the high ash content of the chars; however, on a dry, ash-free basis, the heating values are similar to those of the coals.

A common method for estimating heating values of solid fuels is the Boie equation (Van Krevelan 1961) which permits the heating value to be estimated from the ultimate analysis. The Boie equation has been used to estimate the HHV of the biomass samples in Table 3-4. The average absolute error of the estimate is 4.70%, with a bias of 3.19%. A second method for estimating heating values is that of Tillman (1978). As shown in Table 3-9, the results for Tillman's equation, which uses only the carbon content, give comparable values. The average error is roughly 2.83% with a positive bias of 0.83%.

A third method of estimating gross heating values has been developed at IGT (Institute of Gas Technology 1978) using the experimental heating values and ultimate analyses of more than 700 coal samples. When this heating value correlation is used to estimate the higher heating values of fresh biomass materials, the average error is 3.34% with a negative 1.73% bias.

A linear least-squares regression has been performed on the biomass data set in Table 3-4 and the resulting regression equation is given in Table 3-9. The average error is 2.02%, with a positive bias of 0.09. $R^2$ for the fit is 0.900. A graphical representation of the correlation versus data is given in Figure 3.3. While this better represents the data in Table 3-4, it must be noted that the estimate has not been checked for biomass samples outside the given data set. The experimental error in the ASTM heating value is ± 100 Btu/lb while the regression yields an average error for chars and fresh biomass

of about ± 160 Btu/lb.  Experimental values should be used in cases where the elemental analysis is much different from materials previously tested.

**Table 3-9:  Comparison of Experimental and Calculated Higher (Gross) Heating Values**

| Name | Equation<br><br>HHV [=] Btu/lb | Absolute Avg Error<br>% | Bias<br><br>% | $R^2$ |
|------|----------|----------|----------|----------|
| Boie (1) | 157.4 C + 520.4 H + 28.1 N + 46.9 S - 49.7 O | 4.70 | 3.19 | -- |
| Tillman (2) | 188 C - 718 | 2.83 | 0.83 | -- |
| IGT (3) | 146.58 C + 568.78 H + 29.45 S - 6.58 A - 51.53 (O + N) | 3.34 | -1.73 | -- |
| Bain (4) | 85.65 + 137.04 C + 217.55 H + 62.56 N + 107.73 S + 8.04 O - 12.94 A (Eq 3-15) | 2.02 | 0.09 | 0.900 |

(1)  Van Krevelan, D.W. (1961). <u>Coal; Coal Science and Technology 3,</u> Elsevier Scientific Publishing Company, NY, NY, page 416
(2)  Tillman, D.A. (1978). <u>Wood as an Energy Source</u>, Academic Press, NY, NY.
(3)  Institute of Gas Technology (1978). "Coal Conversion Systems Technical Data Book," DOE Contract EX-76-C-01-2286, available from NTIS.
(4)  This publication

To convert to MJ/kg multiply by 0.00232

Nomenclature: All values are in weight percent, dry basis

> A = ash
> C = carbon
> H = hydrogen
> N = nitrogen
> O = oxygen
> S = sulfur

% Error = 100 (calc. HHV - Exptl. HHV) / Exptl. HHV

Absolute Average Error = $\sum$(absoute error)$_i$ / n

Bias = $\sum$ (Error)$_i$ / n

where n =175

**Figure 3-3: Biomass Higher Heating Value**



Biomass Higher Heating Value

(with 95% confidence interval)
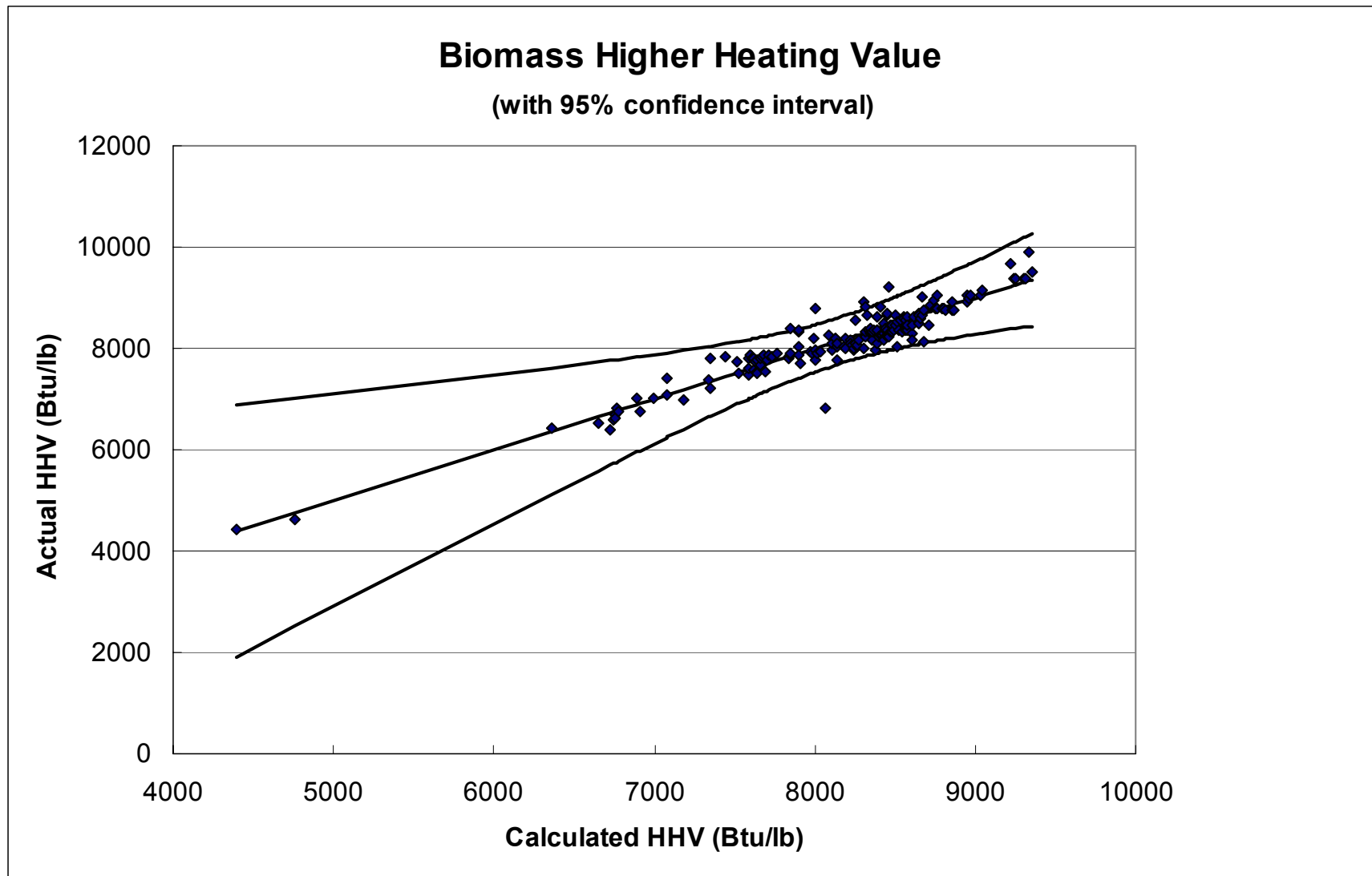
## 3.1.5  Heats of Formation

In thermodynamic calculations, the heat of formation of the feedstocks is required. Heats of formation may be calculated rigorously from the heats of combustion, assuming that the only materials oxidized are C, H, N, and S, by posing the following reactions:

$$\rightarrow CO_2, \qquad \text{-94,052 cal/mole} \qquad\qquad (3\text{-}16)$$

$$\rightarrow H_2O\ (L), \quad \text{-68,317 cal/mole} \qquad\qquad (3\text{-}17)$$

$$\text{Fuels} + O_2$$

$$\rightarrow NO_2, \qquad \text{+7,960 cal/mole} \qquad\qquad (3\text{-}18)$$

$$\rightarrow SO_2, \qquad \text{-70,940 cal/mole} \qquad\qquad (3\text{-}19)$$
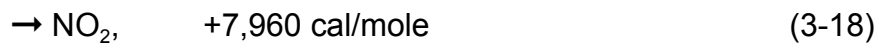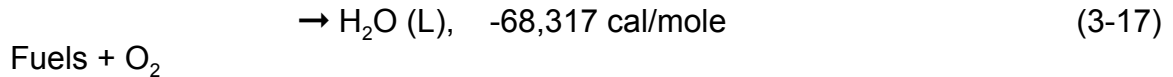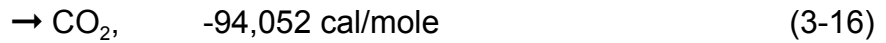
The heat of formation of the fuel may be calculated as follows, assuming no chemical heat involving ash reactions:

$$H_f\ (25°C) = (HHV^* + 0.018 \ \sum\nolimits_{Prod} [\ H_{fi} n_{fi}\ ])\ /\ (1 - Ash) \qquad\qquad (3\text{-}20)$$

in Btu/lb, dry, ash-free basis.

In this equation, $n_{fi}$ is the moles of species i formed per 100 lb of dry biomass on combustion (i can be $CO_2$, $H_2O(L)$, $NO_2$, $SO_2$) while $H_{fi}$ is the heat of formation of i at 25°C in cal/mole.  The factor 0.018 puts the formation enthalpy on a Btu per pound of biomass basis.  The HHV is treated as a positive number.  The heat of formation is normalized to a dry, ash-free basis for purposes of comparison.  Table 3-10 presents heat of formation for a variety of feedstocks.  The data show a definite trend in terms of the rank (degree) of aromatization of the materials involved.  Biomass is very low in rank since its structure consists of only single aromatic rings (benzene derivatives). Fuels of higher rank - peat, lignite, bituminous, and anthracite coals - have structures containing progressively larger aromatic clusters.  Typical bituminous coal structures contain from four to six condensed aromatic rings.  The fuel of highest rank is graphite. The coals tend to have low heats of formation which increase in the exothermic sense as the rank decreases.  Most woody materials exhibit a constant heat of formation in the range of -2,200 Btu/lb.  Materials such as straw and rice hulls have higher heats of formation, on the order of -2,700 Btu/lb.  The biomass chars generally exhibit heats of formation intermediate between coals and fresh biomass materials.  Figure 3-4 shows how the heats of formation depend on the H/C ratio of the feedstock.  It is evident that the biomass chars, although similar in ultimate analysis to coals do not correlate with the coals in terms of H/C ratio.  This is probably due to the coal's greater degree of aromatization, which is a result of the coalification process.

## Table 3-10: Heats of Formation for Typical Fuels and Biomass Materials
(Basis: Dry, Ash-Free Solid)

| Material | Hf (77°F) (Btu/lb) | H'/C' |
|---|---|---|
| Charcoal | 142 | 0.46 |
| Pittsburgh seam coal | -209 | 0.79 |
| Western Kentucky No. 11 coal | -323 | 0.82 |
| Utah coal | -540 | 0.92 |
| Wyoming Elkol | -648 | 0.88 |
| Lignite | -1062 | 0.78 |
| Douglas fir | -2219 | 1.45 |
| Doulas fir bark | -2081 | 1.26 |
| Pine bark | -2227 | 1.33 |
| Western hemlock | -2106 | 1.38 |
| Redwood | -2139 | 1.33 |
| Beech | -2480 | 1.45 |
| Hickory | -2344 | 1.57 |
| Maple | -2203 | 1.43 |
| Poplar | -2229 | 1.45 |
| Rice hulls | -2747 | 1.78 |
| Rice straw | -2628 | 1.56 |
| Sawdust pellets | -1860 | 1.65 |
| Animal waste | -2449 | 1.55 |
| Muncipal solid waste | -2112 | 1.51 |
| Fir bark char | -1580 | 0.96 |
| Muncipal solid waste char | -1136 | 0.87 |
| Grass straw char | -1581 | 0.87 |
| Animal waste char | -1536 | 0.76 |
| Municipal solid waste char | -214 | 0.18 |

**Figure 3-4: Heats of Formation of Carbonaceous Fuels**



Hf = -190.3 - 1407 (H/C), R2 = 0.86
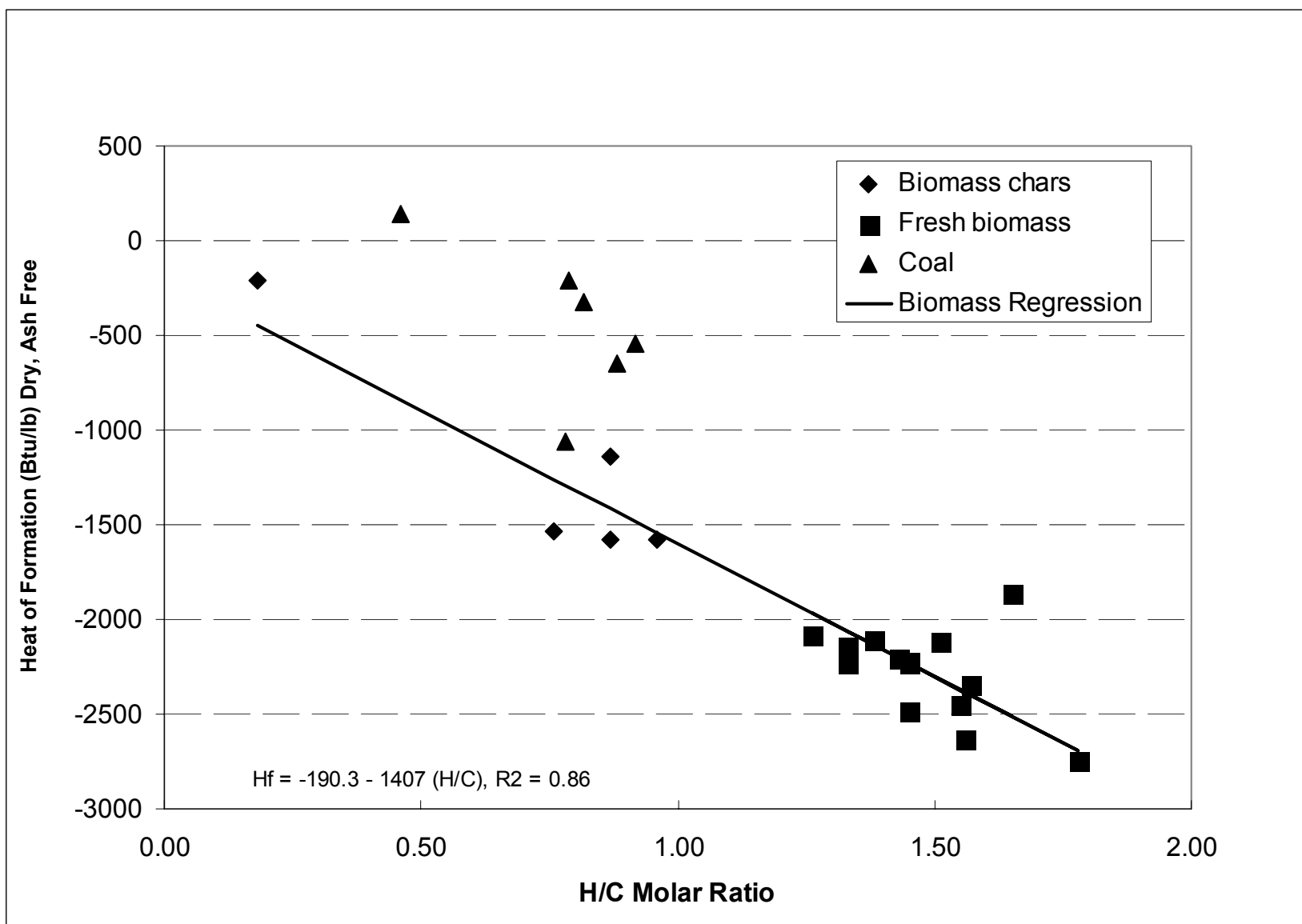
Heats of combustion for biomass materials can be calculated using the heat of formation data based on the following empirical correlation for biomass materials:

$$H_f (77° \ F) = - 190.3 – 1407 \ H'/C' \qquad (3\text{-}21)$$

with H'/C' as mole ratio, Btu/lb, dry ash-free basis.

For natural biomass materials and their chars, the following equation results, based on the ultimate analysis and the pertinent combustion reactions:

$$HHV^* = (141C + 615H - 10.2N + 39.8S) - (1 - A/100)[(16,769H/C) + 190] \qquad (3\text{-}22)$$

The HHV* is the gross heating value on a dry basis, Btu/lb, and the analytical data are expressed in weight percent. This equation cannot be expected to function for manmade materials such as plastics or for non-cellulose-derived materials like leather. For the biomass data set in Table 3-4, the average absolute error is 2.52% and the bias is -0.47%.


## 3.1.6  Ash

The ash content of selected biomass samples in given in Table 3-11.  Biomass with high annual growth, such as herbaceous materials, annual crops, and woody prunings all have abundant alkali in the ash.  Potassium is of primary importance because it volatilizes and reacts during combustion. In addition, biomass rich in both potassium and chlorine can cause large amounts of slagging and fouling during combustion. Biomass ash samples are typically low in sodium content because sodium is toxic to non-halophytic plants.  Ash samples high in iron typically indicate presence of non-biomass materials such as dirt or soil.

## Table 3-11: Ash Composition of Selected Biomass Samples

| Material | Ash wt% | Elemental Composition, wt% | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | SiO2 | Al2O3 | TiO2 | Fe2O3 | CaO | MgO | Na2O | K2O | SO3 | P2O5 | CO2/Other | Undet. |
| Mixed waste paper | 8.33 | 28.10 | 52.56 | 4.29 | 0.81 | 7.49 | 2.36 | 0.53 | 0.16 | 1.70 | 0.20 | | 1.80 |
| Fir mill waste | 0.41 | 15.17 | 3.96 | 0.27 | 6.58 | 11.90 | 4.59 | 23.50 | 7.00 | 2.93 | 2.87 | 18.92 | 2.31 |
| RFD - Tacoma | 26.13 | 33.81 | 12.71 | 1.66 | 5.47 | 23.44 | 5.64 | 1.19 | 0.20 | 2.63 | 0.67 | | 12.58 |
| Red oak sawdust | 0.31 | 20.97 | 2.99 | 0.27 | 2.94 | 10.90 | 4.15 | 1.40 | 22.40 | 2.69 | 1.33 | 14.30 | 15.66 |
| Sugar Cane Bagasse | 2.44 | 46.61 | 17.69 | 2.63 | 14.14 | 4.47 | 3.33 | 0.79 | 4.15 | 2.08 | 2.72 | | 1.39 |
| Urban wood waste | 5.54 | 55.12 | 12.49 | 0.72 | 4.51 | 13.53 | 2.93 | 3.19 | 4.78 | 1.92 | 0.88 | | -0.07 |
| Willow - SV1-3 yr | 0.95 | 8.08 | 1.39 | 0.06 | 0.84 | 45.62 | 1.16 | 2.47 | 13.20 | 1.15 | 10.04 | 13.67 | 2.32 |
| Furniture waste | 3.61 | 57.62 | 12.23 | 0.50 | 5.63 | 13.89 | 3.28 | 2.36 | 3.77 | 1.00 | 0.50 | | -0.78 |
| Willow - SV1-1 yr | 1.10 | 16.76 | 3.01 | 0.07 | 0.85 | 34.83 | 2.46 | 3.05 | 12.20 | 1.70 | 10.36 | 17.58 | -2.87 |
| Alder/fir sawdust | 4.13 | 35.36 | 11.54 | 0.92 | 7.62 | 24.90 | 3.81 | 1.71 | 5.75 | 0.78 | 1.90 | 1.85 | 3.86 |
| Switchgrass, MN | 2.69 | 61.64 | 1.32 | 0.19 | 1.08 | 11.11 | 4.86 | 0.64 | 8.24 | 0.80 | 3.09 | | 7.03 |
| Hybrid poplar | 2.70 | 5.90 | 0.84 | 0.30 | 1.40 | 49.92 | 18.40 | 0.13 | 9.64 | 2.04 | 1.34 | 8.18 | 1.91 |
| Switchgrass, D Leaf, MN | 3.61 | 61.23 | 0.57 | 0.37 | 0.79 | 12.06 | 5.42 | 0.43 | 7.63 | 1.11 | 3.56 | | 6.83 |
| Demolition wood | 13.12 | 45.91 | 15.55 | 2.09 | 12.02 | 13.51 | 2.55 | 1.13 | 2.14 | 2.45 | 0.94 | | 1.71 |
| Forest residuals | 3.97 | 17.78 | 3.55 | 0.50 | 1.58 | 45.46 | 7.48 | 2.13 | 8.52 | 2.78 | 7.44 | | 2.78 |
| Poplar - coarse | 1.60 | 0.88 | 0.31 | 0.16 | 0.57 | 44.40 | 4.32 | 0.23 | 20.08 | 3.95 | 0.15 | 19.52 | 5.43 |
| Miscanthus, Silberfeder | 3.05 | 61.84 | 0.98 | 0.05 | 1.35 | 9.61 | 2.46 | 0.33 | 11.60 | 2.63 | 4.20 | | 4.95 |
| Wood - land clearing | 16.50 | 65.77 | 14.84 | 0.55 | 5.27 | 5.78 | 1.81 | 2.70 | 2.19 | 0.36 | 0.66 | 0.45 | -0.38 |
| Almond wood | 6.78 | 45.60 | 10.75 | 0.54 | 4.06 | 18.96 | 4.22 | 3.08 | 6.26 | 2.06 | 1.47 | | 3.00 |
| Wood - yard waste | 20.37 | 59.65 | 3.06 | 0.32 | 1.97 | 23.75 | 2.15 | 1.00 | 2.96 | 2.44 | 1.97 | | 0.73 |
| Danish wheat straw | 3.89 | 55.32 | 0.84 | 0.22 | 1.05 | 12.27 | 2.48 | 1.51 | 12.90 | 2.49 | 4.30 | | 6.62 |
| Rice husks | 20.26 | 91.42 | 0.78 | 0.02 | 0.14 | 3.21 | 0.01 | 0.21 | 3.71 | 0.72 | 0.43 | | |
| Switchgrass, OH | 8.97 | 65.18 | 4.51 | 0.24 | 2.03 | 5.60 | 3.00 | 0.58 | 11.60 | 0.44 | 4.50 | | 2.32 |
| Oregon wheat straw | 4.32 | 46.07 | 1.69 | 0.09 | 1.85 | 9.95 | 2.45 | 1.18 | 25.20 | 4.92 | 3.32 | | 3.28 |
| Alfalfa stems | 5.27 | 5.79 | 0.07 | 0.02 | 0.30 | 18.32 | 10.38 | 1.10 | 28.10 | 1.93 | 7.64 | 14.80 | 11.55 |
| California wheat straw | 7.02 | 55.32 | 1.88 | 0.08 | 0.73 | 6.14 | 1.06 | 1.71 | 25.60 | 4.40 | 1.26 | | 1.82 |
| Imperial wheat straw | 9.55 | 37.06 | 2.23 | 0.17 | 0.84 | 4.91 | 2.55 | 9.74 | 21.70 | 4.44 | 2.04 | | 14.32 |
| Rice straw | 18.67 | 74.67 | 1.04 | 0.09 | 0.85 | 3.01 | 1.75 | 0.96 | 12.30 | 1.24 | 1.41 | | 2.68 |
| Bana Grass, HI | 9.88 | 33.65 | 0.80 | 0.07 | 0.63 | 3.57 | 1.71 | 0.38 | 42.80 | 0.85 | 2.74 | 8.97 | 3.83 |

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## 3.2    CHEMICAL COMPOSITION OF WOODS

In characterizing and correlating reactivity data for pyrolysis and gasification, it is necessary to have some idea of the chemical structure of the reactant material.  Woods can be analyzed in terms of fractions of differing reactivity by solvent extraction techniques.  This discussion provides some of the relevant information on the structure and composition of these reactive fractions which will be useful in discussions of gasification kinetics and pyrolysis.

Woods can be separated into three fractions: extractables, cell wall components, and ash.  The extractables, generally present in amounts of 4% to 20%, consist of materials derived from the living cell.  The cell wall components, representing the bulk of wood, are principally the lignin fraction and the total carbohydrate fraction (cellulose and hemicellulose) termed holocellulose.  Lignin, the cementing agent for the cellulose fibers, is a complex polymer of phenylpropane.  Cellulose is a polymer formed from d (+)-glucose while the hemicellulose polymer is based on other hexose and pentose sugars.  In woods, the cell wall fraction generally consists of lignin/cellulose in the ratio 43/57.  Residues of the total wood, such as bark and sawdust, have differing compositions.

Table 3-12 presents some analyses of woods on a dry basis while Table 3-13 presents data for typical wood barks.

**Table 3-12: Chemical Analyses of Representative Woods [a]**
(wt % Dry Basis)

| Sample | Ash | Extractables | Lignin | Holocellulose |
|---|---|---|---|---|
| Softwoods[b] | | | | |
|     Western white pine | 0.20 | 13.65 | 26.44 | 59.71 |
|     Western yellow pine | 0.46 | 15.48 | 26.65 | 57.41 |
|     Yellow cedar | 0.43 | 14.39 | 31.32 | 53.86 |
|     Incense cedar | 0.34 | 20.37 | 37.68 | 41.60 |
|     Redwood | 0.21 | 17.13 | 34.21 | 48.45 |
| Hardwoods[c] | | | | |
|     Tanbark oak | 0.83 | 16.29 | 24.85 | 58.03 |
|     Mesquite | 0.54 | 23.51 | 30.47 | 45.48 |
|     Hickory | 0.69 | 19.65 | 23.44 | 56.22 |

[a]Encyclopedia of Chem. Tech. (1963), p. 358
[b]Softwood refers to conifer woods
[c]Hardwood refers to deciduous woods

**Table 3-13: Chemical Analyses of Representative Wood Barks [a]**
(% Dry Basis)

| Sample | Ash | Extractables | Lignin | Holocellulose[b] |
|---|---|---|---|---|
| Black spruce | 2.1 | 24.78 | 45.84 | 24.78 |
| Fir | 3.1 | 30.37 | 39.16 | 27.37 |
| White birch | 1.5 | 21.6 | 37.8 | 39.1 |
| Yellow birch | 2.9 | 19.9 | 36.5 | 40.7 |
| Beech | 8.3 | 18.3 | 37.0 | 36.4 |

[a]From Wise 1946
[b]By difference

In comparing the ultimate analysis data for barks and whole woods in Table 3-4, there is no indication that the chemical makeup of the feedstocks is different.  However, from the extractable and cell wall analyses it is evident that the lignin and extractable contents of barks are much greater than those of whole woods.  It should be expected that these materials would exhibit different overall reactivities due to their chemical differences.

### 3.2.1  Cellulose

The carbohydrate fraction of plant tissues is composed of cellulose and hemicelluloses, which are moderate to high molecular weight polymers based on simple sugars.  Cellulose itself is derived from d-glucose while the hemicelluloses are principally polymers of d-xylose and d-mannose.  The hemicellulose composed of pectin generally is present in only very small quantities in woody material but can be a substantially abundant constituent of the inner bark of trees.  The cellulose polymer is shown in Fig. 3-5.
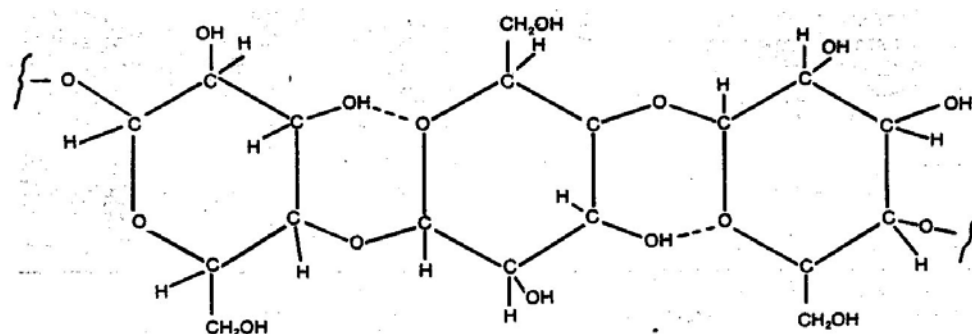


**Figure 3-5:  The Cellulose Molecule**

Cellulose is composed of d-glucose units ($C_6H_{10}O_5$) bound together by ether-type linkages called glycosidic bonds. Glucose is a hexose, or six carbon sugar. In wood the polymers form thread-like chains of molecular weight greater than 100,000. In cotton, 3000 or more units with a combined molecular weight of 500,000 may be present in chains, yielding an extended length of 15,700 Å and cross section of 4 by 8 Å. These very long, thin molecules can be coiled and twisted but, because of the arrangement of the ether linkage, the chain is stiff and extended. An additional contribution to rigidity results from the hydrogen bonding between a hydroxyl hydrogen and the ring oxygen in the adjacent monomer. The threads are woven amongst each other in a random fashion, termed amorphous cellulose, and also fitted together in a crystalline arrangement. Strong van der Waals forces and hydrogen bonds between threads (termed secondary bonding) give rise to a lamellae structure, The weakest bond in the chain direction is the C-O glycosidic bond with an energy of 50 kcal. Cellulose fibers are thus very strong.

The dominant physical characteristic of cellulose is its extreme insolubility, which retards not only acid and enzymic hydrolysis but also the removal of lignins and hemicelluloses interspersed through the cellulose structures. The strong secondary bonding is responsible for the insolubility. Cellulose can be dissolved by strong acids such as hydrochloric, sulfuric, and phosphoric.

Pyrolysis of cell wall materials provides a mixture of volatile materials, tars, and char. The proportion of each fraction and its composition depends on the reaction conditions including temperature, pressure, heating rate, and atmospheric composition. Char results from the condensation of aromatic compounds formed from the primary decomposition products. Since aromatics are not present initially, the amount of char formed by condensation reactions is relatively small.

### 3.2.2  Principal Hemicelluloses

Interlaced with cellulose in the cell walls are a number of other polymeric sugars termed hemicelluloses. These are generally differentiated from true cellulose by their solubility in weak alkaline solutions. Figure 3-6 shows a sequence employed by Timell (1967) for isolating softwood polysaccharides. Hemicelluloses are not precursors of cellulose; they are distinctly different compounds that contain acidic and neutral molecules of low and high molecular weight. In contrast to cellulose, which appears to be universal and invariant as the structural polysaccharide of higher land plants, the hemicellulose polysaccharides show a significant variation in composition and structure among species. Several reviews of hemicellulose chemistry have been presented by Polglase (1955), Aspinall (1959), and Whistler and Richards (1970).

Most hemicelluloses contain two to four (and occasionally five to six) simpler sugar residues, d-xylose, d-glucose, d-mannose, d-galactose, 1-arabinose, d-glucuronic acid, and 4-O-methyl-d-glucuronic acid residues constitute the majority of hemicellulose monomers as shown in Fig. 3-7. The structure is similar to that of cellulose except that
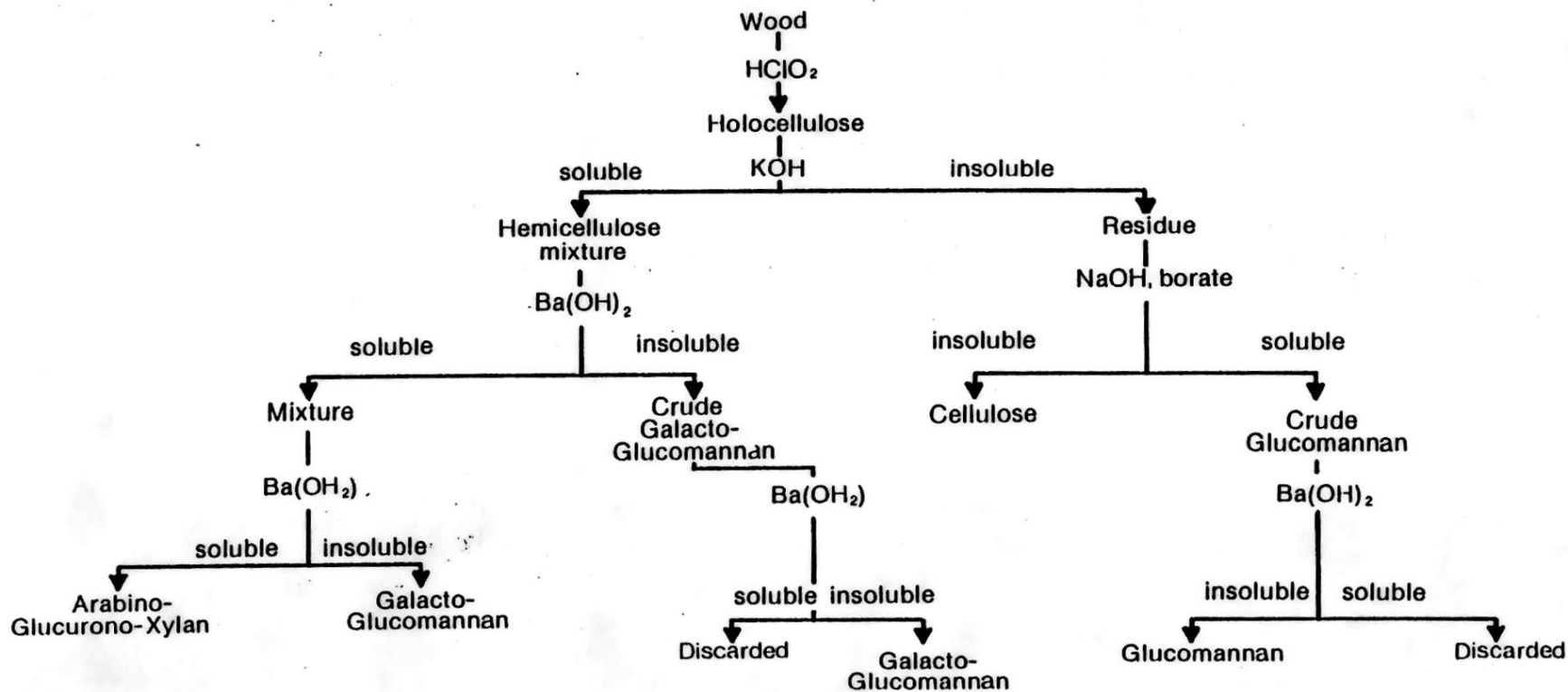
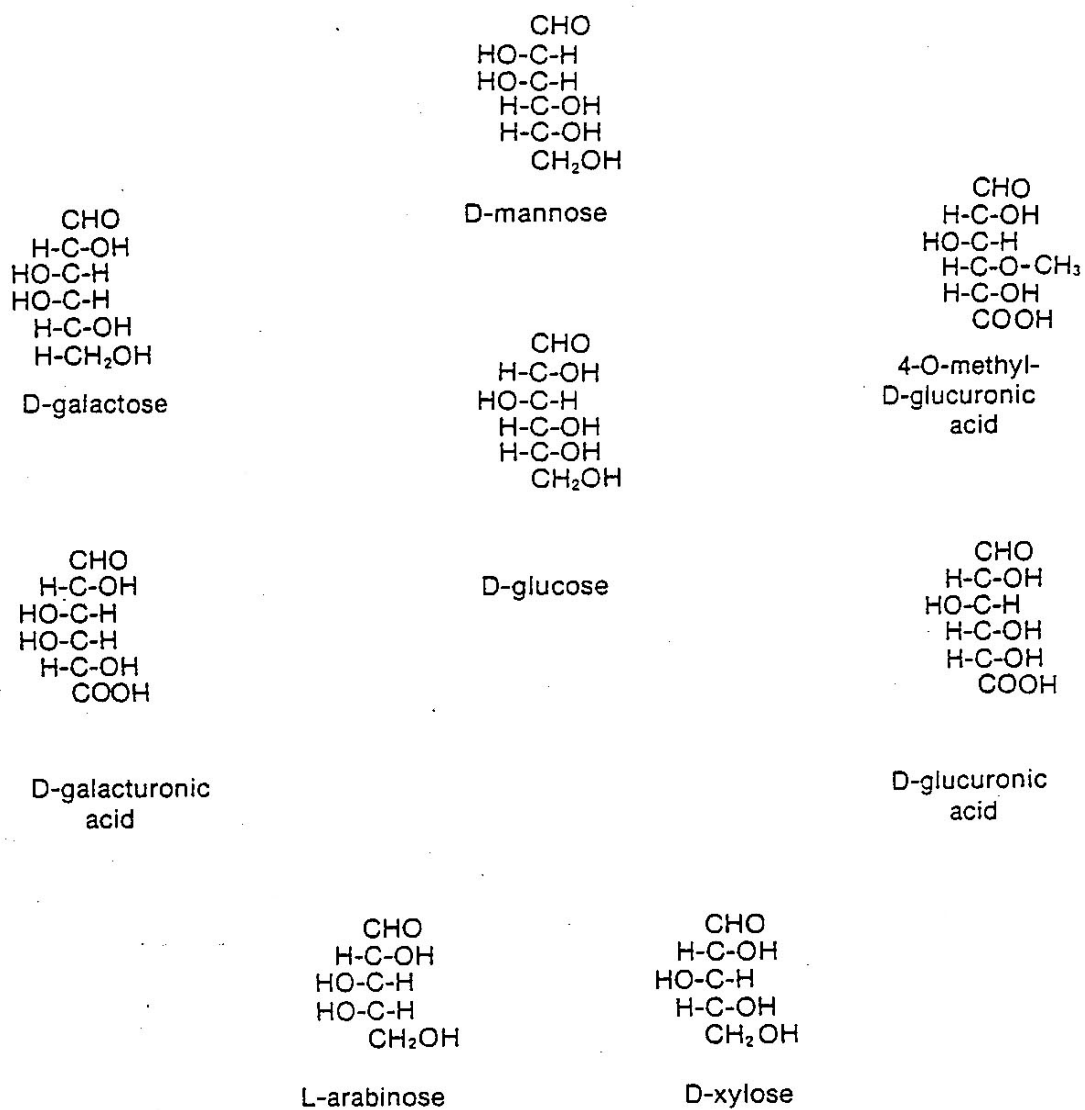**Figure 3-6: Extraction Sequence for Isolation of Softwood Polysaccharides**

CHO
HO-C-H
HO-C-H
H-C-OH
H-C-OH
CH₂OH

D-mannose

CHO
H-C-OH
HO-C-H
HO-C-H
H-C-OH
H-CH₂OH

D-galactose

CHO
H-C-OH
HO-C-H
H-C-OH
H-C-OH
CH₂OH

D-glucose

CHO
H-C-OH
HO-C-H
H-C-O-CH₃
H-C-OH
COOH

4-O-methyl-
D-glucuronic
acid

CHO
H-C-OH
HO-C-H
HO-C-H
H-C-OH
COOH

D-galacturonic
acid

CHO
H-C-OH
HO-C-H
H-C-OH
H-C-OH
COOH

D-glucuronic
acid

CHO
H-C-OH
HO-C-H
HO-C-H
CH₂OH

L-arabinose

CHO
H-C-OH
HO-C-H
H-C-OH
CH₂OH

D-xylose

**Figure 3-7: Structural Interrelationship of Commonly Occurring Hemicellulose Component Sugars**

the hemicellulose polymers generally contain 50 units to 200 units and exhibit a branched rather than a linear structure.

These structural characteristics, as well as the number and proportion of different sugar residues present (degree of heteropolymerization), largely determine the observed physical properties of hemicelluloses.  The heteropolymerization decreases the ability to form regular, tight-fitting crystalline regions and thus makes hemicellulose more soluble than cellulose.  Solubility is also increased due to the branching, which decreases the number of intermolecular hydrogen bonds, and the decreased degree of polymerization compared to cellulose.

### 3.2.2.1      Xylans

Xylans, the most abundant of the hemicelluloses, are polymers of d-xylose ($C_5H_{10}O$). Xylose is a pentose sugar.  The xylan fraction of cellulose is often termed pentosan. They are most abundant in agricultural residues such as grain hulls and corn stalks. Hardwoods (deciduous) and softwoods contain appreciable amounts of xylans.  Xylan chains are short, exhibiting molecular weights on the order of 30,000 or less.  In addition, some xylans contain carboxylic acid and methyl-ether groups.  Typical xylans are shown in Fig. 3-8.  The acidic xylans contain d-glucuronic acis or the methylate acid as terminal branch units.

Some of the acid xylans are of low molecular weight.  They are known as hemicellulose-B and are differentiated from the normal xylans and other neutral hemicelluloses in that they are not precipitated from the alkaline extract by neutralization.

### 3.2.2.2      Mannans

Mannan-based hemicelluloses include glucomannans, which are built up from linked d-glucose and d-mannose residues in about a 30:70 ratio, and galactoglucomannans, made up of linked d-galactose, d-glucose, and d-mannose in 2:10:30 ratios.  In softwoods, mannans are present in substantial amounts while in hardwoods there is generally very little mannan hemicellulose.

### 3.2.3  Cellulose Data for Woods

Table 3-14 presents some data on the cellulose content of woods.  The holocellulose fraction of hardwoods is composed principally of cellulose and xylans.  The total content of mannans and other hemicelluloses averages only 4.8% for the four samples.  In softwoods, the cellulose fraction is about the same as in hardwoods.  However, mannans are present to a much greater extent; the mannans equal or exceed the total xylans in the conifers.  Other hemicelluloses are present at 5.4% on the average for the four samples.
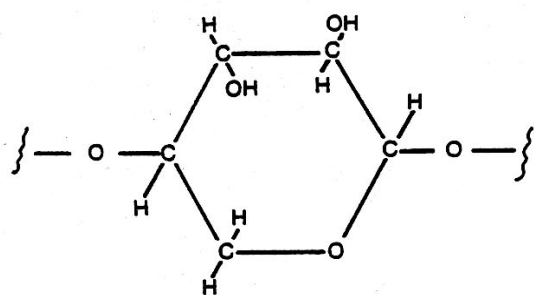
Xylan
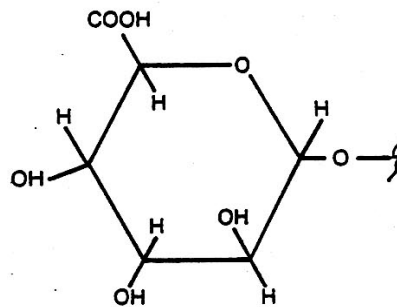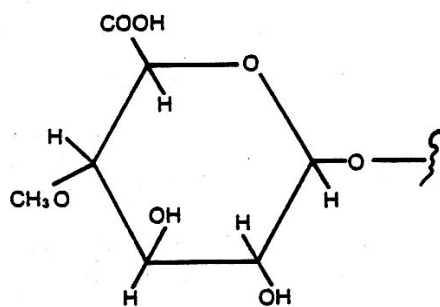
Acid Xylans-Terminal Groups

**Figure 3-8: Xylan Hemicellulose Structures**

**Table 3-14: Breakdown of Holocellulose Fraction of Woods** [a]

| | Wt% in Holocellulose | | | | |
| --- | --- | --- | --- | --- | --- |
| | Cellulose | Xylans | Acidxylans | Mannans | Others |
| Hardwoods | | | | | |
|     Trembling Aspen | 71.5 | 20.0 | 4.1 | 2.9 | 1.5 |
|     Beech | 64.5 | 23.8 | 6.5 | 2.9 | 2.3 |
|     Sugar Maple | 69.8 | 20.0 | 5.9 | 3.1 | 1.2 |
|     Southern Red Oak | 59.8 | 28.3 | 6.6 | 2.9 | 2.4 |
| Softwoods | | | | | |
|     Eastern hemlock | 69.0 | 6.1 | 5.0 | 17.1 | 2.8 |
|     Douglas Fir | 64.6 | 4.2 | 4.2 | 16.0 | 11.0 |
|     White spruce | 65.2 | 9.5 | 5.0 | 16.3 | 3.9 |
|     Jack Pine | 65.1 | 10.1 | 5.6 | 15.1 | 4.0 |

[a]From Encyclopedia of Chem. Tech., 1963, p. 358.

### 3.2.4  Lignin

The noncarbohydrate component of the cell wall, termed lignin, is a three-dimensional polymer based primarily on the phenylpropane unit.  Lignin is deposited in an amorphous state surrounding the cellulose fibers and is bound to the cellulose directly by ether bonds.  Its exact structure is not known, although considerable information is available based on its chemical reactivity.  In solubility analyses, lignin is defined as the cell wall portion not soluble in 72% sulfuric acid.  Table 3-15 gives typical elemental analyses of wood lignins.

**Table 3-15: Elemental Analysis of Wood Lignin**

| Type | C (%) | H (%) | O(%) | $OCH_3$ (%) | Molecular Wt. |
| --- | --- | --- | --- | --- | --- |
| Softwood | 63.8 | 6.3 | 29.9 | 15.8 | 10,000 |
| Hardwood | 59.8 | 6.4 | 33.7 | 21.4 | 5,000 |

It is assumed, based on much evidence, that the lignins are composed of several monomer groups as shown in Fig. 3-9.  These are combined to form the polymer by a variety of linkages involving the aromatic rings and functional groups.  The polymer formed contains only single aromatic rings as shown in 3-10 (structural formula).
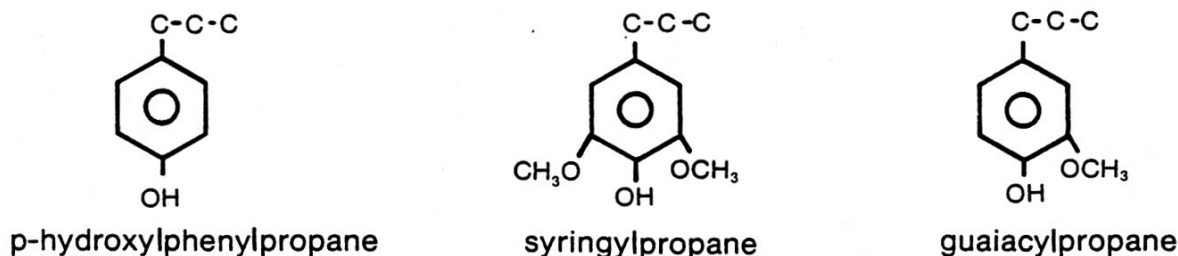
**Figure 3-9: Several Monomer Units in Lignin**

The representative structure contains the phenylpropane substituted as sinapyl, coniferyl, and p-coumaryl alcohols as shown in Fig. 3-11. Lignification, as discussed by Freudenberg (1965), is thought to occur by dehydration-ploymerization of these alcohol units. Thermal pyrolysis of lignin generally yields a considerable amount of char. It is likely that thermal pyrolysis and lignification follow the same route to yield a condensed polynuclear aromatic structure.

The amount of lignin present varies among materials. Typical amounts for woods and barks are given in Tables 3-12 and 3-13. Table 3-16 gives data for a variety of other biomass materials.

**Table 3-16: Lignin in Miscellaneous Plant Material [a]**

| Material | Wt %, Dry Unextracted Material |
|---|---|
| Rice hulls | 40.0 |
| Bagasse | 20.3 |
| Peanut shells | 28.0 |
| Pine needles | 23.9 |
| Wheat straw | 13.9 |
| Corncobs | 13.4 |

[a] From Encyclopedia of Chem. Tech., 1963, p.361

### 3.2.5 Extractables

The nature and quantity of extractables vary widely among woods. Table 3-17 lists the type of extractables found in a variety of wood materials. The resins and volatile oils

are fragrant and found most commonly in softwoods.  Waxes, fatty acids, pigments, and carbohydrates are commonly found in all woods.  Starches account for about 3% of the total wood.  Since the quality and nature of extractables vary, the products after pyrolysis and gasification vary.

**Table 3-17: Extractable Components of Wood**

Volatile Oils (removed by steam of ether soluble

      Terpenes ($C_{12}H_{16}$)

      Sesquiterpene ($C_{15}H_{24}$)
           and their oxygenated derivatives

Resins and Fatty Acids (soluble in ether)

      Resin acids ($C_{20}H_{30}O_2$)

      Fatty acids (oleic, linoleic, palmitic)

      Glyceryl esters of fatty acids

      Waxes (esters of monohydroxyalcohols and fatty acids)

      Physterols (high molecular weight cyclic alcohols)

Pigments (soluble in alcohol)

      Flavonols (multi-ring naphthenic and aromatic alcohols, chlorides, ketones acids)

      Pyrones (multi-ring naphthenic and aromatic alcohols, chlorides, ketones acids)

      Antranols  (multi-ring naphthenic and aromatic alcohols, chlorides, ketones acids

      Tannins (amorphous polyhydroxylic phenols)

Carbohydrate Components (water soluble)

      Starch

      Simple sugars
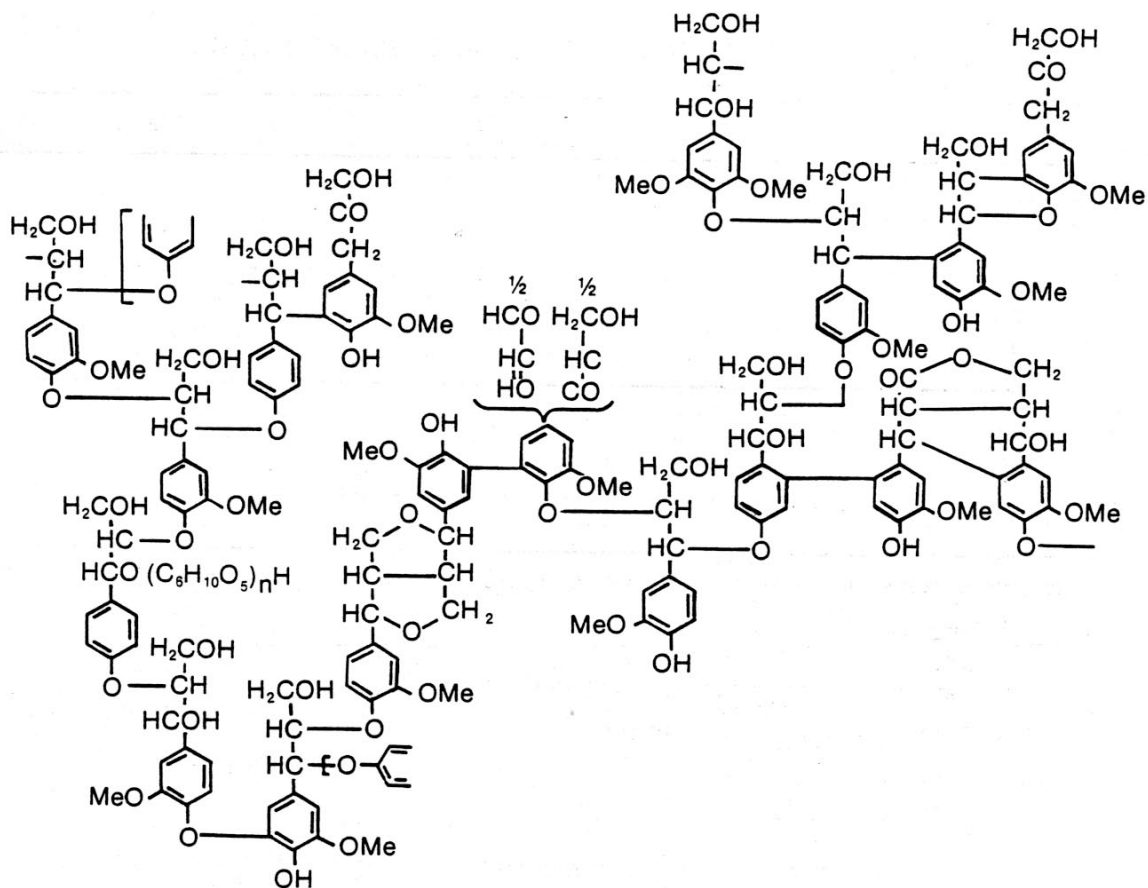
      Organic acids

**Figure 3-10: Representative Structure of Coniferous Lignin**



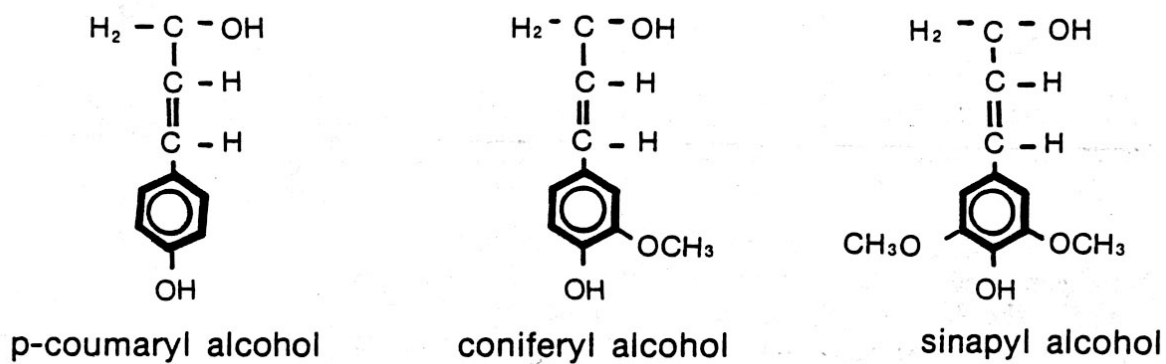p-coumaryl alcohol      coniferyl alcohol      sinapyl alcohol

**Figure 3-11: P-Hydroxycinnamyl Alcohols**

Table 3-18 presents some typical extraction data on woods. The bulk of the extractables may be removed by hot water and ether. The ether-soluble portion is usually much greater for the softwoods, showing the higher content of volatile oils and resins. The hot water extraction, which leaches some tannins as well as the carbohydrates, gives yields approximately the same for the soft- and hardwoods.

**Table 3-18: Extraction Data for Woods [a]**

| Sample | Wt % of Solubles | |
| --- | --- | --- |
| | Hot Water | Ether |
| Softwoods | | |
|     Western yellow pine | 5.05 | 8.52 |
|     Yellow cedar | 3.11 | 2.55 |
|     Incense cedar | 5.38 | 4.31 |
|     Redwood | 9.86 | 1.07 |
|     Western white pine | 4.49 | 4.26 |
|     Longleaf pine | 7.15 | 6.32 |
|     Douglas fir | 6.50 | 1.02 |
|     Western larch | 12.59 | 0.81 |
|     White spruce | 2.14 | 1.36 |
| Hardwoods | | |
|     Tanbark oak | 5.60 | 0.80 |
|     Mesquite | 15.09 | 2.30 |
|     Hickory | 5.57 | 0.63 |
|     Basswood | 4.07 | 1.96 |
|     Yellow birch | 3.97 | 0.60 |
|     Sugar Maple | 4.36 | 0.25 |
| Average—Softwoods | 6.25 | 3.36 |
| Average—Hardwoods | 6.44 | 1.09 |

[a]From Enclyclopedia of Chem. Tech., 1963, p.358

## 3.3    WOOD STRUCTURE

Wood is composed of cells of various sizes and shapes.  Long pointed cells are known as fibers; hardwood fibers are about 1mm in length, while softwood fibers vary in length from about 3mm to 8mm.  The mechanical properties of wood depend largely on its density, which, in turn, is largely determined by the thickness of the cell walls.

### 3.3.1  Physical Structure of Softwoods

Figure 3-12 shows a typical softwood structure taken from Siau (1971).  In softwoods, the fluid conducting elements are the longitudinal tracheids and ray tracheids.  Longitudinal and horizontal resin canals are also present in many species.

Longitudinal tracheids, shown in Fig. 3-13, make up the bulk of the structure of softwoods.  These are long, hollow, narrow cells having no openings that are tapered along the radial surfaces for a considerable portion of the lengths where they are in contact with other tracheids.  The surfaces of the tracheids are dotted with pits, minute depressions in the plant tissue wall which permit the movement of water and dissolved materials between tracheids.  The pit is covered with a semipermeable membrane.  Pits are oriented in softwoods as adjacent pairs (pit pairs); fluid flow occurs between tracheids in the direction normal to the principal direction of flow.

The tracheid diameter varies from 15 to 80 μm according to species, with a length ranging from 1200 to 7500 μm.  Average values of diameter and length, respectively, are 33 μm and 3500 μm.  The inner diameter which is available for flow is typically 20-30 μm.  The effective radius of the pit openings is 0.01 to 4 μm due to the restriction created by the membrane.  Typically, a tracheid contains 50 pits.  In addition to pit pairs allowing longitudinal flow, there are also pit pairs leading from longitudinal tracheids to ray tracheids, permitting radial flow.

The volumetric composition of a typical softwood is as follows:

| | |
|---|---|
| Longitudinal tracheids | 93% |
| Longitudinal resin canals | 1% |
| Ray tracheids | 6% |

Since the principal voidage is oriented longitudinally, the magnitude of the permeability in the longitudinal direction is much greater than the radial permeability.  Figure 3-14 shows a schematic model for flow through a softwood.

### 3.3.2  Physical Structure of Hardwoods

The structure of a typical hardwood is shown in Fig. 3-15. The dominant feature of the hardwood structure is the large open vessels or pores. Tracheids and pits are present but contribute significantly more resistance to flow. In a typical hardwood, the following structural composition is present:

|           |     |
|-----------|-----|
| Vessels   | 55% |
| Tracheids | 26% |
| Woods rays| 18% |
| Others    | 1%  |

Vessels are large, with diameters of 20 to 30 μm. The vessels are short, connected by "perforation plates" which offer very low flow resistance. Thus the vessels behave as long capillaries. Figure 3-16 shows the nature of flow through hardwoods.
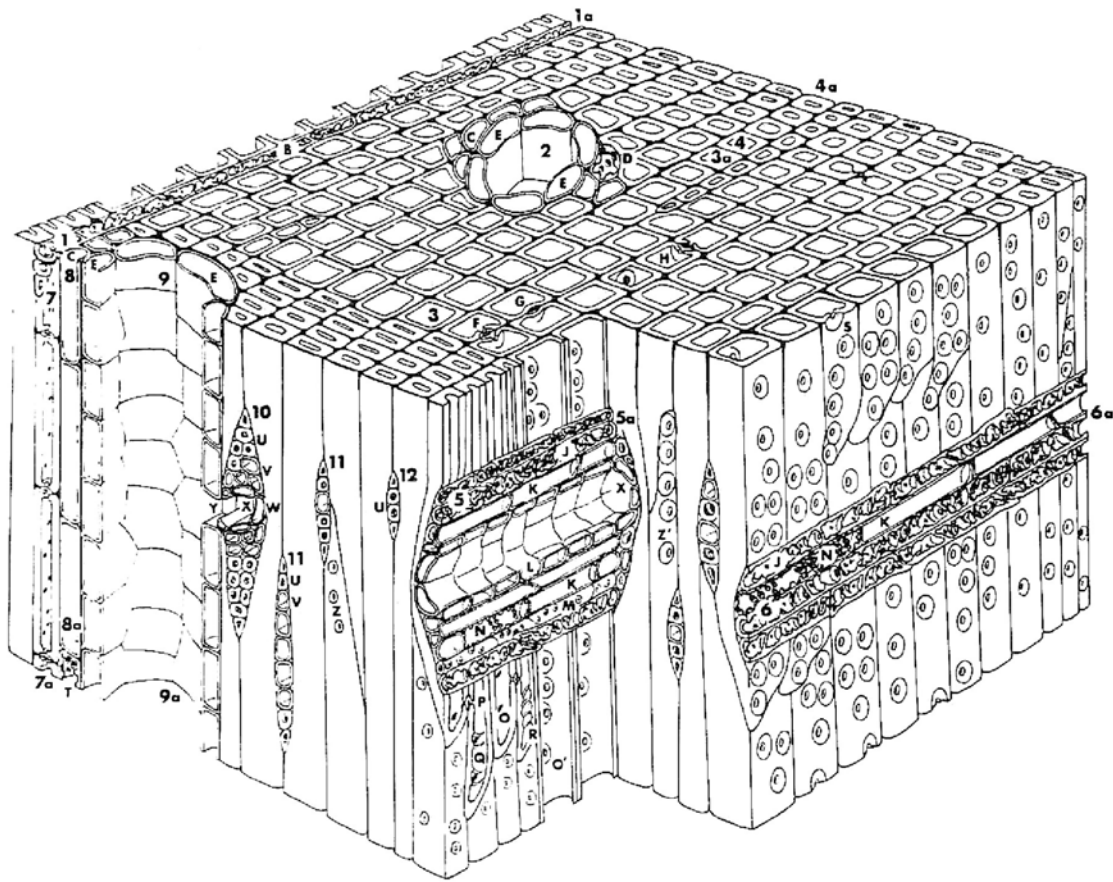
**Figure 3-12: Gross Structure of a Typical Southern Pine Softwood**

Transverse view: 1-1a, ray; B, dentate ray tracheid; 2, resin canal; C, thin-walled longitudinal parenchyma; D, thick-walled longitudinal parenchyma; E, epithelial cells; 3-3a, earlywood tracheids; F, radial bordered pit pair cut through torus and pit apertures; G, pit pair cut below pit apertures; H, tangential pit pair; 4-4a, latewood.

Radial view: 5-5a, sectioned fusiform ray; J, dentate ray tracheid; K, thin-walled parenchyma; L, epithelial cells; M, unsectioned ray tracheid; N, thick-walled parenchyma; O, latewood radial pit (inner aperture); O', earlywood radial pit (inner aperture); P, tangential bordered pit; Q, callitorid-like thickenings; R, spiral thickenings; S, radial bordered pits (the compound middle lamella has been stripped away removing crassulae and tori); 6-6a, sectioned uniseriate heterogenous ray.

Tangential view: 7-7a, strand tracheids; 8-8a, longitudinal parenchyma (thin-walled); T, thick-walled parenchyma; 9-9a, longitudinal resin canal; Y, opening between horizontal and vertical resin canals; 11, uniseriate homogeneous rays; 12, uniseriate homogeneous ray; Z, small tangential pits in latewood; Z', large tangential pits in earlywood.
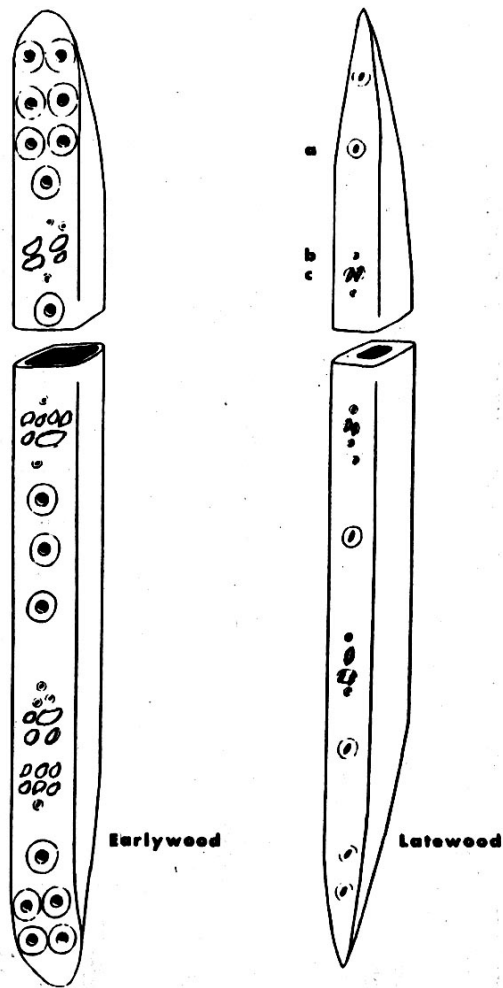
**Figure 3-13:  Radial Surfaces of Earlywood and Latewood Tracheids**

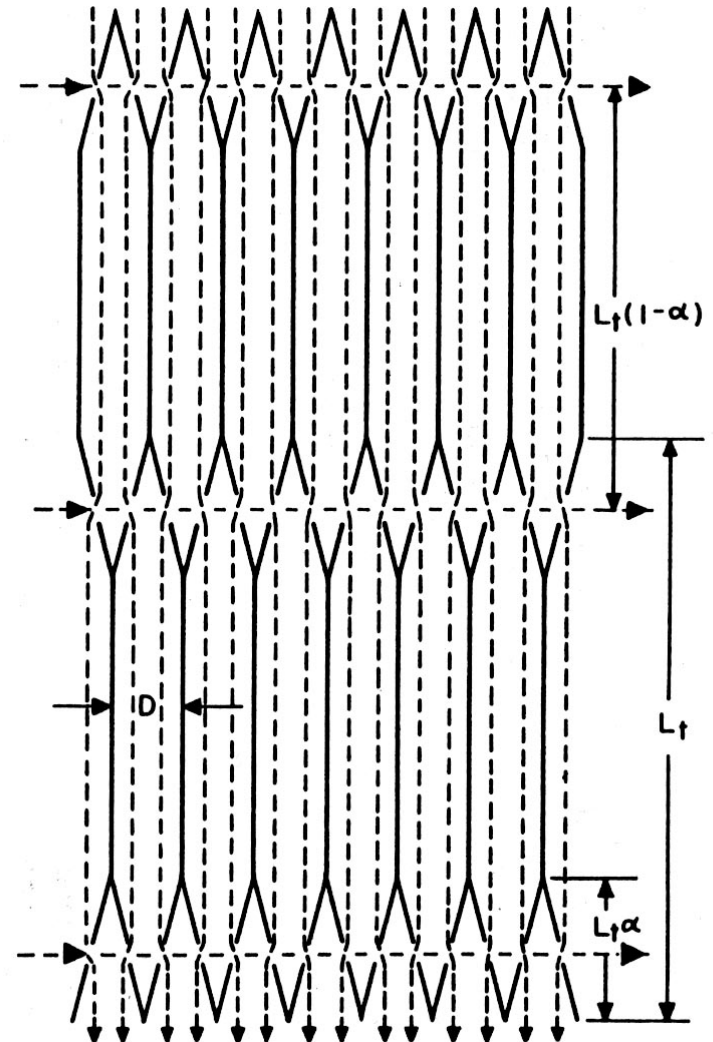(a) intertracheal bordered pits; (b) bordered pits to tracheids; (c) pinoid pits to ray parenchyma



**Figure 3-14: Softwood Flow Model**
Tangential section showing pits on the radial surfaces
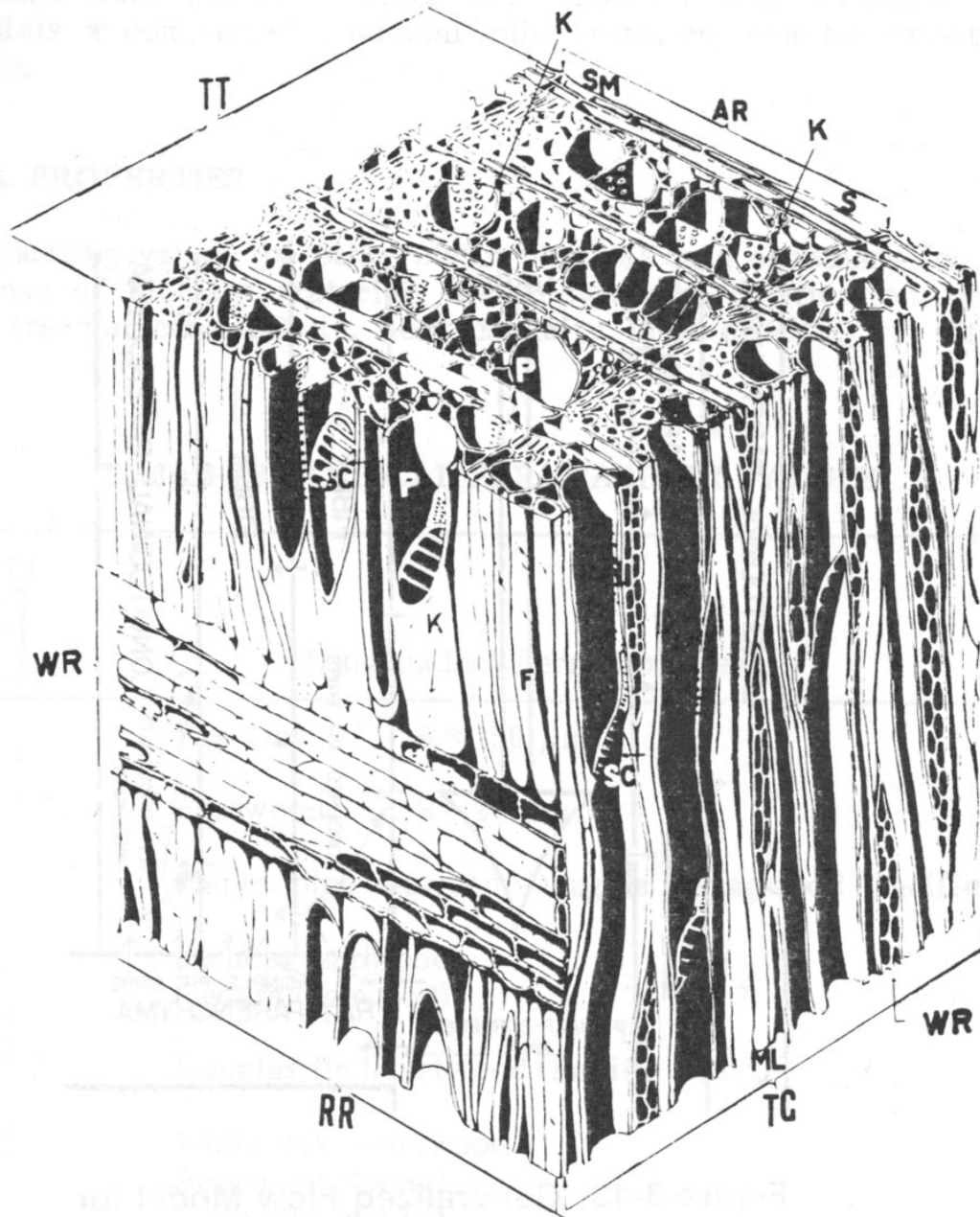Of the tapered ends of the tracheids

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**Figure 3-15: Gross Structure of a Typical Hardwood**

Plane TT is the cross section, RR is the radial surface, and TG is the tangential surface. The vessels or pores are indicated by P, and the elements are separated by scalariform perforation plates, SC. The fibers, F, have small cavities and thick walls. Pits in the walls of the fibers and vessels, K, provide for the flow of liquid between the cells, The wood rays are indicated at WR. AR indicates one annual ring. The earlywood (springwood) is designated S, while the latewood (summerwood) is SM. The true middle lamella is located at ML.
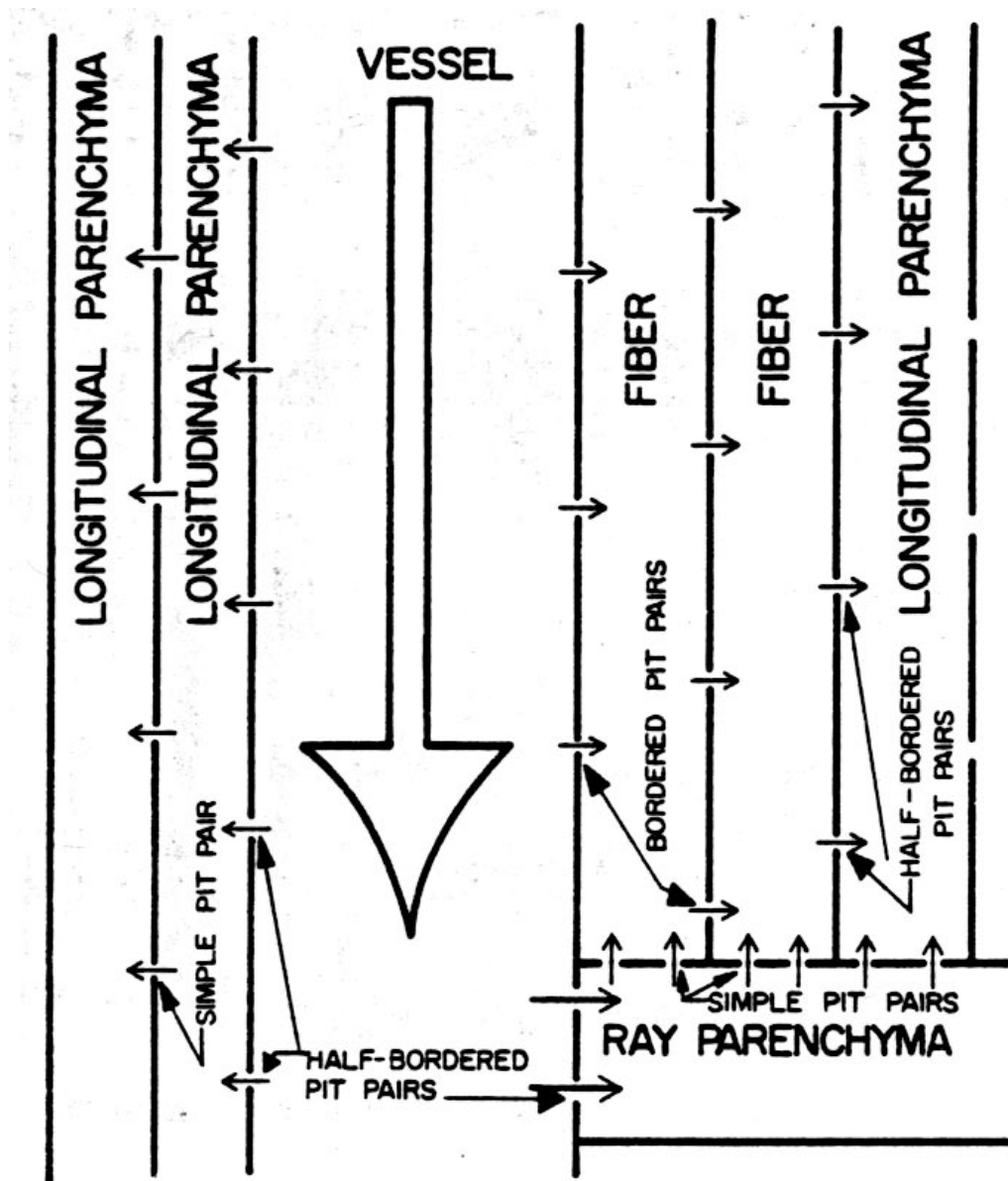
**Figure 3-16: Generalized Flow Model for Hardwoods**

### 3.3.3 Permeability

Permeability is important in pyrolysis. During heating, pyrolysis gases and liquids are generated within the particle and must pass through the porous structure to the surroundings. Low permeability may significantly affect the product distribution by increasing the residence time of the primary pyrolysis products in the hot zone, thereby increasing the probability that they will enter into secondary reactions. Pelletized, densified biomass will have a low permeability compared with natural woods. Table 3-19 shows the range of permeability for various natural woods.

In natural soft- and hardwood structures, it is evident that the porosity is directed principally in the vertical direction in the livewood. Physical properties such as thermal conductivity and diffusivity therefore depend on direction within fresh wood. Such a behavior is termed anisotropic (aeolotropic).

**Table 3-19: Typical Permeability Values**

| Permeability $(cm^3 (air)cm^{-1}atm^{-1})$ | Longitudinal Permeabilities | |
|---|---|---|
| $10^4$ | Red Oak | $R \approx 150$ μm |
| $10^3$ | Basswood | $R \approx 20$ μm |
| $10^2$ | Maple, oine sapwood, Douglas fir sapwood (Pacific Coast) | |
| $10^1$ | Spruces (sapwood), cedars (sapwood) | |
| $10^0$ | Douglas fir heartwood (Pacific Coast) | |
| $10^{-1}$ | White oak heartwood, Beech heartwood, Cedar heartwood | |
| | Douglas fir heartwood (intermountain) | |
| $10^{-2}$ | | Transverse permeabilities. (The species are in approximately the same order as for longitudinal permeabilties) |
| $10^{-3}$ | | |
| $10^{-4}$ | | |

## 3.4    PHYSICAL PROPERTIES

In addition to heating value, the other major physical data necessary for predicting the thermal response of biomass materials under pyrolysis, gasification, and combustion processes are thermal conductivity, heat capacity, true density, and diffusion coefficients.

### 3.4.1  **Thermal Conductivity**

Thermal conductivity is defined in general terms as a proportionality factor which relates heat flow through a material to a temperature difference across a specified distance in that material.  Mathematically, thermal conductivity is defined by Fourier's Law of Heat Conduction, given here for unidimensional heat flux in the x-direction in rectangular coordinates:

$$q_x = -k_x \frac{dT}{dx} \qquad (3\text{-}23)$$

Most homogeneous materials are isotropic, and the thermal conductivity varies only with temperature

$$q = -k\nabla T \qquad (3\text{-}24)$$

However, most naturally occurring biomass materials are anisotropic.  For wood, the thermal conductivity is a function of temperature and spatial direction.  Modified biomass materials, such as densified wood, probably do not exhibit the same type of anisotropic behavior as the naturally occurring biomass materials.  Thermal conductivity should be related to the various materials present in a substance.  Thus in biomass thermal conductivity should be a function of the major constituents, including moisture, cellulose, hemicellulose, and lignin.

Table 3-20 compiles available thermal conductivity data for biomass materials.  No data are available for compacted biomass feedstocks.  In general, no chemical analyses are presented with the data.  The bulk of the data are probably effective thermal conductivities of powders rather than of the solids.  The conductivities for solid woods, for example, are two to ten times greater than for many of the other biomass materials listed in Table 3-20 (e.g., sawdust and redwood shavings).  Most data sources do not specify the state of the materials.

Steinhagen (1977) has summarized thermal conductivity data for several woods over the range -40° C to +100° C as a function of moisture content and has shown that moisture is an important parameter in wood conductivity.  Since the moisture content is not known for the bulk of the entries in Table 3-20, the data presented are at best only semi-quantitative.

Completely lacking in the available data are thermal conductivities at higher temperatures. This is primarily because the majority of the data were determined by researchers in the forest products industry interested in the thermal properties of wood and insulating materials for home heating and cooling applications.  If thermal conductivity values are to be used in modeling pyrolysis or gasification processes, then new data over the actual range of processing conditions must be developed, including data for densified materials.

## Table 3-20: Thermal Conductivity of Selected Biomass Materials

| Material | Bulk Density (lb/ft³) | Temperature (°F) | Thermal Conductivity (Btu/ft-h-°F) | Reference |
|---|---|---|---|---|
| Ashes, wood | -- | 32 - 212 | 0.040 | Kern 1950 |
| Cardboard | -- | -- | 0.037 | Kern 1950 |
| Carbon, porous, with grain | | | | |
|     Grade 60    48% porosity | 65.5[a] | Room Temp. | 0.083 | Perry and Chilton 1973 |
|     Grade 45    47% porosity | 64.9 | Room Temp. | 0.083 | Perry and Chilton 1973 |
|     Grade 25    47% porosity | | Room Temp. | 0.083 | Perry and Chilton 1973 |
| Carbon Refractory brick - 17% porosity | | Room Temp. | 1.33 | Perry and Chilton 1973 |
| Celotex, sheet fiber from sugar cane | 13.2 | -- | 0.028 | Handbook Chem. Phys, 1966 |
| | 14.8 | -- | 0.028 | Handbook Chem. Phys, 1966 |
| | 14.4 | 32 | 0.0253 | McAdams 1954 |
| | 14.4 | 0 | 0.0242 | McAdams 1954 |
| | 14.4 | -100 | 0.0208 | McAdams 1954 |
| | 14.4 | -200 | 0.0175 | McAdams 1954 |
| | 14.4 | -300 | 0.0133 | McAdams 1954 |
| Charcoal - from maple, beech, birch | | | | |
|     Coarse | 13.2 | -- | 0.030 | Handbook Chem. Phys, 1966 |
|     6 mesh | 15.2 | -- | 0.031 | Handbook Chem. Phys, 1966 |
|     20 mesh | 19.2 | -- | 0.032 | Handbook Chem. Phys, 1966 |
| Charcoal flakes | 11.9 | 176 | 0.043 | McAdams 1954 |

| Material | Bulk Density (lb/ft³) | Temperature (°F) | Thermal Conductivity (Btu/ft-h-°F) | Reference |
|---|---|---|---|---|
| | 15 | 176 | 0.051 | McAdams 1954 |
| | -- | 0 to 100 | 0.0133 | Handbook Chem. Phys, 1966 |
| Cork, regranulated | | | | |
| Fine particles | 9.4 | -- | 0.025 | Handbook Chem. Phys, 1966 |
| 1/16-in. Particles | 8.1 | -- | 0.026 | Handbook Chem. Phys, 1966 |
| Corkboard | 5.4 | -- | 0.021 | Handbook Chem. Phys, 1966 |
| | 7.0 | -- | 0.022 | Handbook Chem. Phys, 1966 |
| | 10.6 | -- | 0.025 | Handbook Chem. Phys, 1966 |
| | 14.0 | -- | 0.028 | Handbook Chem. Phys, 1966 |
| | 6.9 | 32 | 0.0205 | McAdams 1954 |
| | 6.9 | 0 | 0.0200 | McAdams 1954 |
| | 6.9 | -100 | 0.0183 | McAdams 1954 |
| | 6.9 | -200 | 0.0142 | McAdams 1954 |
| | 6.9 | -300 | 0.0100 | McAdams 1954 |
| Cork, pulverized | 10.0 | 32 | 0.035 | McAdams 1954 |
| | 10.0 | 100 | 0.039 | McAdams 1954 |
| | 10.0 | 200 | 0.032 | McAdams 1954 |
| Cotton | 5.0 | 200 | 0.037 | McAdams 1954 |
| | 5.0 | 100 | 0.035 | McAdams 1954 |
| | 5.0 | 32 | 0.0325 | McAdams 1954 |
| | 5.0 | -100 | 0.0276 | McAdams 1954 |

| Material | Bulk Density (lb/ft$^3$) | Temperature (°F) | Thermal Conductivity (Btu/ft-h-°F) | Reference |
|---|---|---|---|---|
| | 5.0 | -200 | 0.0235 | McAdams 1954 |
| Cotton | 5.0 | -300 | 0.0198 | McAdams 1954 |
| Graphite - 2 ¾" Dia., ¾ " Thick, 30% porosity | 98.6[a] | -- | 7.33 | Handbook Chem. Phys, 1966 |
|     Porous, Grade 60 52% porosity | 65.5[a] | -- | 4.17 | Handbook Chem. Phys, 1966 |
|     Porous, Grade 45 53% porosity | 64.9[a] | -- | 3.75 | Handbook Chem. Phys, 1966 |
|     Porous, Grade 25 53% porosity | 64.3[a] | -- | 3.33 | Handbook Chem. Phys, 1966 |
| Paper | -- | -- | 0.075 | McAdams 1954 |
| Paper or pulp, macerated | 2.5-3.5 | -- | 0.0121 | Lewis 1968 |
| Sawdust, various | 12.0 | -- | 0.034 | Handbook Chem. Phys, 1966 |
|     Redwood | 10.9 | -- | 0.035 | Handbook Chem. Phys, 1966 |
|     (and shavings) | 8-15 | -- | 0.0375 | Handbook Chem. Phys, 1966 |
| Sawdust (soft pine and oak) | | | | |
|     10 - 40  mesh | -- | -295 | 0.016 | Chow 1948 |
| | -- | -180 | 0.0195 | Chow 1948 |
| | | -105 | 0.0235 | Chow 1948 |
| | | -55 | 0.0265 | Chow 1948 |
| | | -20 | 0.0295 | Chow 1948 |
| | | 5 | 0.0325 | Chow 1948 |
| | | 30 | 0.0355 | Chow 1948 |
| | | 35 | 0.0385 | Chow 1948 |
| | | 62 | 0.040 | Chow 1948 |

| Material | Bulk Density (lb/ft³) | Temperature (°F) | Thermal Conductivity (Btu/ft-h-°F) | Reference |
|---|---|---|---|---|
| ªApparent density, defined in Section 3.4.3 | | | | |
| Shredded redwood bark | 4.0 | 32 | 0.0290 | McAdams 1954 |
| | 4.0 | -100 | 0.0235 | McAdams 1954 |
| | 4.0 | -200 | 0.0196 | McAdams 1954 |
| | 4.0 | -300 | 0.0155 | McAdams 1954 |
| | -- | -50 | 0.0168 | Rowley et al. 1945 |
| | -- | -25 | 0.0180 | Rowley et al. 1945 |
| | -- | 25 | 0.0203 | Rowley et al. 1945 |
| | -- | 75 | 0.0226 | Rowley et al. 1945 |
| Sheet insulite, from wood pulp | 16.2 | -- | 0.028 | Handbook Chem. Phys, 1966 |
| | 16.9 | -- | 0.028 | Handbook Chem. Phys, 1966 |
| Wood fiber, mat | 1.7 | -50 | 0.016 | Rowley et al. 1945 |
| | 1.7 | 0 | 0.018 | Rowley et al. 1945 |
| | 1.7 | 50 | 0.020 | Rowley et al. 1945 |
| | 1.7 | 100 | 0.023 | Rowley et al. 1945 |
| Wood fiber, blanket | 3.5 | -50 | 0.016 | Rowley et al. 1945 |
| | 3.5 | 0 | 0.018 | Rowley et al. 1945 |
| | 3.5 | 50 | 0.020 | Rowley et al. 1945 |
| | 3.5 | 100 | 0.022 | Rowley et al. 1945 |
| Wood fiber, excelsier | 1.64 | -50 | 0.019 | Rowley et al. 1945 |
| | 1.64 | 0 | 0.022 | Rowley et al. 1945 |

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| Material | Bulk Density (lb/ft$^3$) | Temperature (°F) | Thermal Conductivity (Btu/ft-h-°F) | Reference |
|---|---|---|---|---|
| | 1.64 | 50 | 0.022 | Rowley et al. 1945 |
| Wood fiber, excelsier | 1.64 | 100 | 0.024 | Rowley et al. 1945 |
| Solid woods | | | | |
| Balsa | 8 - 12 | -300 | 0.0151 | Gray et al. 1960 |
| | 8 - 12 | -285 | 0.0150 | Gray et al. 1960 |
| | 8 - 12 | -260 | 0.0167 | Gray et al. 1960 |
| | 8 - 12 | -207 | 0.0183 | Gray et al. 1960 |
| | 8 - 12 | -190 | 0.0192 | Gray et al. 1960 |
| | 8 - 12 | -160 | 0.0233 | Gray et al. 1960 |
| | 8 - 12 | -130 | 0.0233 | Gray et al. 1960 |
| | 8 - 12 | -95 | 0.0232 | Gray et al. 1960 |
| Balsa, across grain | 7.3 | -- | 0.028 | Handbook Chem. Phys, 1966 |
| | 8.8 | -- | 0.032 | Handbook Chem. Phys, 1966 |
| | 20 | -- | 0.048 | Handbook Chem. Phys, 1966 |
| Cypress, across grain | 29 | -- | 0.056 | Handbook Chem. Phys, 1966 |
| Mahogany, across grain | 34 | -- | 0.075 | Handbook Chem. Phys, 1966 |
| Maple, across grain | 44.7 | 122 | 0.11 | McAdams 1954 |
| Fir | 26 | 75 | 0.063 | Chapman 1974 |
| Oak | 30 - 38 | 86 | 0.096 | Chapman 1974 |
| Yellow pine | 40 | 75 | 0.065 | Chapman 1974 |
| White pine | 27 | 86 | 0.087 | Chapman 1974 |

| Material | Bulk Density (lb/ft$^3$) | Temperature (°F) | Thermal Conductivity (Btu/ft-h-°F) | Reference |
|---|---|---|---|---|
| Pine, white, across grain | 34 | 59 | 0.087 | McAdams 1954 |
| | 32 | -- | 0.032 | Handbook Chem. Phys, 1966 |
| Pine, Virginia, across grain | 34 | -- | 0.082 | Handbook Chem. Phys, 1966 |
| Pine board, 1 ¼" thick | -- | -50 | 0.0515 | Gray et al. 1960 |
| | -- | 0 | 0.054 | Gray et al. 1960 |
| | -- | 50 | 0.0575 | Gray et al. 1960 |
| | -- | 100 | 0.059 | Gray et al. 1960 |
| Pine, with grain | 34.4 | 59 | 0.20 | McAdams 1954 |
| Oak, across grain | 51.5 | 59 | 0.12 | McAdams 1954 |

Equations have been developed for wood, expressing thermal conductivity as a function of of moisture and specific gravity for combined heat flow in the radial and tangential directions (McLean 1941).  The expression was derived at ambient temperatures.

For moisture contents less than 40% the thermal conductivity is expressed as

$$k = S(0.116 + 0.00233M) + 0.01375 \qquad (3\text{-}25)$$

and for moisture contents greater than 40%

$$k = S(0.116 + 0.00317M) + 0.01375 \qquad (3\text{-}26)$$

where        S = apparent specific gravity, as defined in Section 3.4.3
                 M = Percent moisture content, oven dry basis, or

$$M = 100(W - D)/D, \qquad (3\text{-}27)$$

where        W = Original weight
                 D = Dry weight after oven drying

A plot of thermal conductivity as a function of moisture content and specific gravity using equation 3-25 is given in Figure 3-17.



Figure 3-17: Thermal Conductivity as a Function of Moisture and Specific Gravity (MacLean 1941)
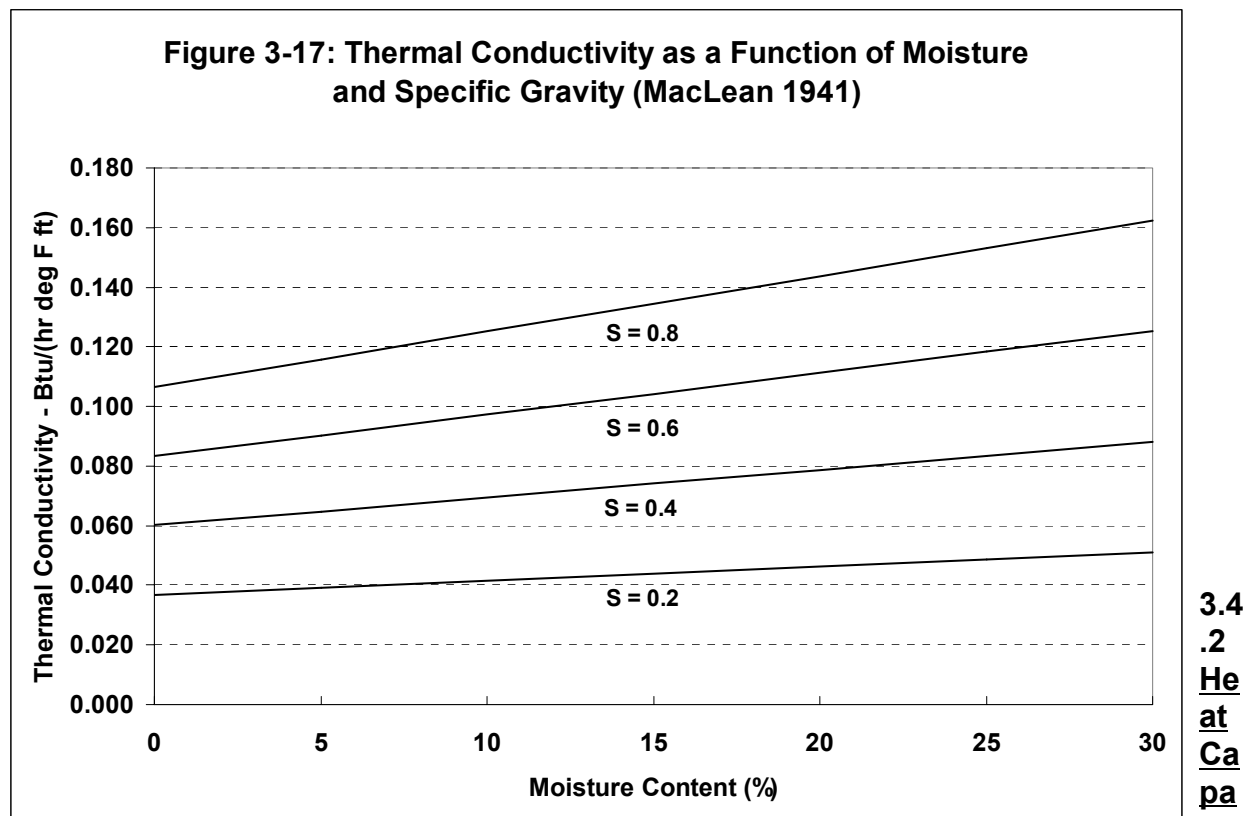
**city**

Heat capacity, as normally reported, is defined in terms of the enthalpy content of a material and represents the relative ability of a material to store energy. Enthalpy is a function of temperature and pressure.

$$H = H(T,P) \tag{3-28}$$

and

$$dH = (\partial H/\partial T)_P \, dT + (\partial H/\partial P)_T \, dP \tag{3-29}$$

For solids and liquids $\partial H/\partial P$ is very small and

$$dH = (\partial h/\partial T)_P \, dT \tag{3-30}$$

By definition the temperature dependency term $(\partial H/\partial P)_p$ is called heat capacity at constant pressure, $C_p$, and is reported on a per unit weight basis. The resulting equation for the enthalpy change is as follows:

$$\Delta H = \int_{T_O}^{T} C_P \, dT \tag{3-31}$$

This equation is normally used for materials of constant mass and no phase transitions. For example, if water is driven out of wood the apparent heat capacity may change very rapidly with temperature; the same is true for other phase transitions. Generally, if phase transitions are incorporated the enthalpy change will be:

$$\Delta H = \int_{T_O}^{T_P} C^\alpha{}_P \, dT \;\; + \;\; \Delta H_{PHASE\ CHANGE} \;\; + \;\; \int_{T_P}^{T} C^\beta{}_P \, dT \tag{3-32}$$

where

$C^a{}_P, C^\beta{}_P$ = heat capacities of phases 1 and 2

$T_P$ = temperature at which phase change occurs

The heat capacity is a function of the composition and temperature but not the density of the material as long as compacting does not alter the chemical structure.

The data on heat capacity are limited. Some typical values are given in Table 3-21. No characterization data are reported for the samples.

Several $C_P$ equations have been developed to predict the heat capacities of wood at temperatures to 100 °C.  As an example of specific heat equations for woods, Beall (1968) shows the equation in which moisture is an important parameter in estimating the heat capacity:

$$C_p = 0.259 + (9.75 \times 10^{-4})M + 6.05 \times 20^{-4}T_1 + 1.3 \times 10^{-5}M\ T_1, \qquad (3\text{-}33)$$

where

M = % moisture, up to 27%.

**Table 3-21: Heat Capacity**

| Material | Temperature (°F) | Heat capacity (Btu lb$^{-1}$ °F$^{-1}$) | Reference |
|---|---|---|---|
| Carbon | 78-168 | 0.168 | Perry 1973 |
| | 103-1640 | 0.314 | Perry 1973 |
| | 132-2640 | 0.387 | Perry 1973 |
| Charcoal | 50 | 0.16 | Perry 1973 |
| Cellulose | -- | 0.32 | Perry 1973 |
| Oak | -- | 0.57 | Perry 1973 |
| Fir | 75 | 0.65 | Chapman 1974 |
| Yellow pine | 75 | 0.67 | Chapman 1974 |
| Cork | 68 | 0.45 | Chapman 1974 |

Other methods are available and generally are for the same temperature range.

As with thermal conductivity, no references were readily available for heat capacity of biomass materials for the temperature range of thermal processing conditions needed for pyrolysis or gasification; new data are needed for applicable temperature ranges.

### 3.4.3  Density

The density of the material is important in considering energy contents of fuels on a volumetric basis, such as for transporting, solids handling, and sizing reaction vessels. There are three ways of reporting solid material density: bulk density, apparent particle

density, and skeletal density. These density values differ in the way in which the material volume is calculated.  The bulk density volume basis includes the actual volume of the solid, the pore volume, and the void volume between solid particles. Apparent particle density includes solid volume and pore volume.  Skeletal density, or true density, includes only solid volume.  The three values are related as follows:

$$\rho_a = \rho_s(1-\epsilon_p) \qquad\qquad (3\text{-}34)$$

$$\rho_b = \rho_a(1-\epsilon_b), \qquad\qquad (3\text{-}35)$$

where

$\rho_s$ = skeletal density, weight/volume
$\rho_a$ = apparent density, weight/volume
$\rho_b$ = bulk density, weight/volume

$\epsilon_p$ = particle porosity = $\dfrac{\text{Volume of pores}}{\text{Volume of pores and volume of solid}}$

$\epsilon_b$ = bed porosity = $\dfrac{\text{Volume of external voids}}{\text{Volume of external voids and volume of particles}}$

Densification of biomass is accomplished by reducing the particle porosity $\epsilon_p$.

The density of biomass depends on the nature of the material, its moisture content, and degree of densification.  Raw, over-dry biomass (with 7% to 8% moisture) has an apparent density of about 40 lb/ft$^3$ (hardwoods) and 28 lb/ft$^3$ (softwoods).  The density of woods with high moisture contents can be as high as 60 lb/ft$^3$.  Densification produces particles with apparent bone dry densities of 55 lb/ft$^3$ to 75 lb/ft$^3$.  The skeletal density of over dry biomass has been reported to be 91 lb/ft$^3$ (Siau 1971).  Bulk densities of a number of biomass materials are given in Table 3-20.  Apparent densities of a number of biomass materials are given in Table 3-22.

### 3.4.3.1    Effect of Moisture Content on Density

The apparent density of wood and biomass depends on the moisture content.  The dry and wet biomass apparent densities are related as follows from the moisture content obtained from the proximate analysis of the raw feedstock:

$$\rho_a(D) = (1-M)\,\rho_a(R), \qquad\qquad (3\text{-}36)$$

where

$\rho_a(D)$ = apparent density of dry biomass,
$\rho_a(R)$ = apparent density of raw biomass, and
    M = proximate moisture.

For a typical raw biomass with 50% moisture and apparent dry density of 30 lb/ft$^3$, the raw biomass sample has a density of 60 lb/ft$^3$.

**Table 3-22: Apparent Density of Selected Woods**
(Jenkins, 1989)

| Wood Type | Specific Gravity | Density (lb/ft$^3$) |
|---|---|---|
| Almond | 0.78 | 48.67 |
| Alder (red) | 0.38 | 23.71 |
| Ash (white) | 0.54 | 33.70 |
| Aspen | 0.36 | 22.46 |
| Bald cypress | 0.43 | 26.83 |
| Beech | 0.57 | 35.57 |
| Birch, yellow | 0.55 | 34.32 |
| Cedar, incense | 0.35 | 21.84 |
| Cottonwood | 0.37 | 23.09 |
| Elm, American | 0.46 | 28.70 |
| Fir, balsam | 0.32 | 19.97 |
| Hemlock, mountain | 0.42 | 26.21 |
| Hickory, pecan | 0.61 | 38.06 |
| Maple, sugar | 0.57 | 35.57 |
| Oak, northern red | 0.56 | 34.94 |
| Oak, white | 0.60 | 37.44 |
| Pine, jack | 0.40 | 24.96 |
| lodgepole | 0.39 | 24.34 |
| ponderosa | 0.39 | 24.34 |
| sugar | 0.34 | 21.22 |
| Poplar, balsam | 0.30 | 18.72 |
| Redwood, old growth | 0.39 | 24.34 |
| Spruce, black | 0.38 | 23.71 |
| Tanoak | 0.58 | 36.19 |
| Yellow poplar | 0.40 | 24.96 |

## 3.4.3.2 Densification

Densification by compaction reduces the internal voidage of the biomass material and reshapes the particles so that the bulk density is increased.  The bulk density of green wood chips is typically 20 lb/ft$^3$, while the apparent density is on the order of 60 lb/ft$^3$. The typical external void fraction, $\epsilon_b$, for chips is therefore about 0.67.  The high voidage is due to the shape of the particles.  Reshaping the particles to cylinders typically reduces the void fraction $\epsilon b$ to about 0.5 and thus raises the bulk density to about 30 lb/ft$^3$.  Thus the weight per unit volume is increased 50% by reshaping, and more material can be transported in the same carrier volume.

Densification of biomass by decreasing the particle porosity further improves handling. For raw, dry biomass of apparent density of 30 lb/ft$^3$, the particle porosity, $\epsilon_p$, is typically 0.67 assuming 91 lb/ft$^3$ for the skeletal density.  For densified samples, with reported apparent bone dry densities of 55 lb/ft$^3$ to 75 lb/ft$^3$, the particle porosity has decreased to 0.4 to 0.18.  Thus in densification a large fraction of the internal voidage is removed.


## 3.4.4  Diffusion Coefficients in Biomass Materials

No data are readily available in the literature on gas diffusion coefficients in either natural or pelleted biomass materials or in the pyrolysis chars.

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